[*Continued*]

PROBLEMS IN ORGANIC CHEMISTRY

FOR ADVANCED STUDENTS

by

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TO THE LATE

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ROYAL INSTITUTE OF SCIENCE, BOMBAY

PREFACE

We know the limitations of this *brochure* which we are offering to the students. Organic Chemistry is a vast field and to deal satisfactorily with all the topics or at least with important topics would require several hundred pages. It is, therefore, requested that this booklct should not be taken as a Treatise or a Text-Book of Problems in Organic Chemistry, but as a mere Help to students of degree classes.

The actual mathematical calculations in solving Organic Chemistry Problems are very few and very simple. They involve finding empirical and molecular formulæ from the percentages of elements or from the given quantities of CO_2, H_2O, silver halides, etc. formed from the known weight of the substance, or sometimes in addition to these, in the case of nitrogen, from the given volume of the gas at a certain temperature and pressure. But finding out the empirical and molecular formulæ is not sufficient to give all the information about a compound. The structure or the constitutional formulæ, (especially in higher examinations) is the final goal; and to determine the structure or constitutional formula, one must be able to interpret correctly the various reactions given. This requires thorough acquaintance with organic compounds, their properties and peculiar reactions, a subject which essentially belongs to Organic Chemistry. We have, however, given in the beginning some important reactions which will help the students to revise their old acquaintances and stimulate their fading memory. In chapter II, are given problems with solutions which will not only demonstrate the correct way of writing answers but will also show the correct method of handling problems. Problems for solutions are given in the last chapter. Except for a few simple examples in the beginning (which are meant solely for recapitulation), examples are generally selected from the question papers set at the B. A., and B. Sc., (both pass and honours) degree examinations of Indian and foreign Universities. Though the selection may appear to be rather arbitrary and the sequence of problems

without any arrangement, we have taken sufficient care to keep up the standard. The want of arrangement of problems has, however, one advantage in this that the student is not allowed to think in a well-set groove of topics, but is required to be alert for any topic at any time.

Our special thanks are due to Mr. V. L. Pradhan of the Fergusson College, Poona, who has unhesitatingly given every kind of help while the book was going through the press; without his willing help, this booklet may not have reached the present stage. We have also to thank Mr. V. S. Kulkarni of the Nowrosjee Wadia College, Poona, for reading the proof sheets and giving valuable suggestions. Lastly we offer our thanks to our printers and the publishers whose most sincere co-operation throughout, has been worthy of special mention.

Poona,
15th Sept, 1948

Authors

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ERRATA

PAGE	LINE	INCORRECT	CORRECT
12	18	ammonia	ammonia or
15	15	RNH : NHR'	RNH · NHR'
15	17	$2C_6H_5NH : NHC_6H_5$	$2C_6H_5NH \cdot NHC_6H_5$
15	*Add the following two lines after line 17 :—* (4) Intra-molecular change, $C_6H_5NH{\cdot}HNC_6H_5 \rightarrow H_2N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$		
19	14	kisselguhr.	kieselguhr.
25	17	0·2736 × 35·5 × 100	0·273 × 35·5 × 100
27	3rd (from bottom)	$C_6H_5NH : NHC_6H_5$	$C_6H_5NH \cdot NHC_6H_5$
28	3	N alkali	N/10 alkali
29	4	44 × 0·358	18 × 0·358
30	7	$NH_2{\cdot}COOH_2$	$NH_2{\cdot}CH_2COOH$
31	13	10·9%	10·8%
32	10	10·9	10·8
36	4	98 × 0·192	18 × 0·192
59	9	derivate	derivative
69	17	100 × 1	100 × 14
70	9th (from bottom)	structure	structures
72	8th (from bottom)	$C_{10}H_{12}O_2$	$C_{10}H_{12}O_3$
75	8	action bromine	action of bromine
75	16	can found	can be found
80	7th (from bottom)	$\begin{matrix}CH_3\\C_2H_5\end{matrix}\rangle C : N \cdot N \cdot OH$	$\begin{matrix}CH_3\\C_2H_5\end{matrix}\rangle C : N \cdot OH$
88	*Add the following between lines 10 and 11 :—* $C_9H_9O_6N\cdot$ (A), on boiling with alkaline potassium permanganate, gave a product of the formula		
88	3rd (from bottom)	3-*o*-nitrophenyl glyconic acid	*o*-nitrophenyl glyceric acid

Problems in Organic Chemistry For Advanced Students

CHAPTER I

ORGANIC REACTIONS

(*1*) *Hydrocarbons.*—(i) Aliphatic : Saturated, Unsaturated. (ii) Aromatic compounds.

(*2*) *Hydroxy compounds.*—Alcohols, Phenols.

(*3*) *Alcohol derivatives.*—Alkyl halides, Ethers, Nitriles.

(*4*) *Carbonyl compounds.*—Aldehydes, Ketones, Quinones.

(*5*) *Acids and acid derivatives.*—Acids, Acyl halides, Anhydrides, Esters, Amides.

(*6*) *Amines.*—Aliphatic, Aromatic.

(*7*) *Aromatic derivatives.*—Sulphonic acid, Nitro compounds, Halogen compounds.

(*8*) *Special reactions.*—Diazo compounds, Grignard's Reagent, Friedel-Craft Reaction.

(*9*) *Reduction.*

(*10*) *Oxidation.*

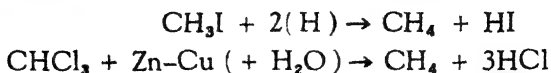
(1) Hydrocarbons

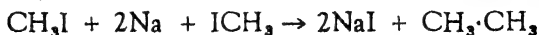
I. Paraffins

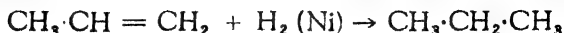
(*A*) *Preparation.*

(i) Reduction of alkyl halides with Zn – Cu couple, mixture of conc. HI + P, or active H,

$$CH_3I + 2(H) \rightarrow CH_4 + HI$$

$$CHCl_3 + Zn\text{–}Cu\ (+ H_2O) \rightarrow CH_4 + 3HCl$$

(ii) Coupling of two alkyl halids—Wurtz's Reaction,

$$CH_3I + 2Na + ICH_3 \rightarrow 2NaI + CH_3{\cdot}CH_3$$

(iii) Reduction of unsaturated linkages with H_2 + catalyst,

$$CH_3{\cdot}CH = CH_2 + H_2\ (Ni) \rightarrow CH_3{\cdot}CH_2{\cdot}CH_3$$

(iv) Distillation of salt with NaOH (Soda lime),

$$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3.$$

(*B*) *Properties.*

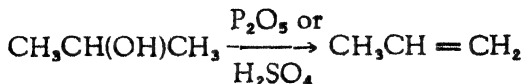
(i) Substitution by chlorine or bromine, but **not** by iodine.

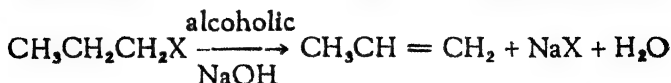
(ii) Inert towards other reagents—e. g. H_2SO_4, HNO_3, NaOH, $KMnO_4$

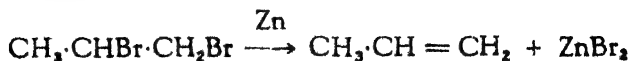
II. Olefines

(*A*) *Preparation,*

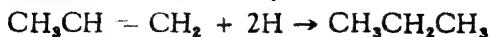
(i) Dehydration.

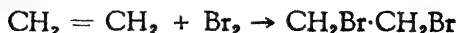
$$CH_3CH(OH)CH_3 \xrightarrow[H_2SO_4]{P_2O_5 \text{ or}} CH_3CH = CH_2$$

(ii) Splitting out H and X (halogen) with alcoholic alkali,

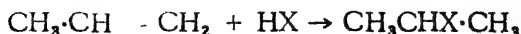
$$CH_3CH_2CH_2X \xrightarrow[NaOH]{\text{alcoholic}} CH_3CH = CH_2 + NaX + H_2O$$

(iii) Removal of two halogen atoms from two adjacent carbon atoms with Zn.

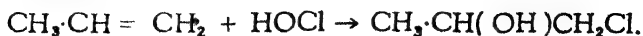
$$CH_3{\cdot}CHBr{\cdot}CH_2Br \xrightarrow{Zn} CH_3{\cdot}CH = CH_2 + ZnBr_2$$

(*B*) *Properties.*

(i) Addition of H_2 (Catalysed)

$$CH_3CH = CH_2 + 2H \rightarrow CH_3CH_2CH_3$$

(ii) Addition of halogens

$$CH_2 = CH_2 + Br_2 \rightarrow CH_2Br{\cdot}CH_2Br$$

(iii) Addition of hydrogen halide yields alkyl halide. The halogen atom goes mainly to the carbon atom with the fewest H atoms (Merkownikoff).

$$CH_3{\cdot}CH = CH_2 + HX \rightarrow CH_3CHX{\cdot}CH_3$$

(iv) Addition of hypochlorous acid (HOCl)

$$CH_3{\cdot}CH = CH_2 + HOCl \rightarrow CH_3{\cdot}CH(OH)CH_2Cl.$$

(v) Cold concentrated sulphuric acid yields alkyl hydrogen sulphate.

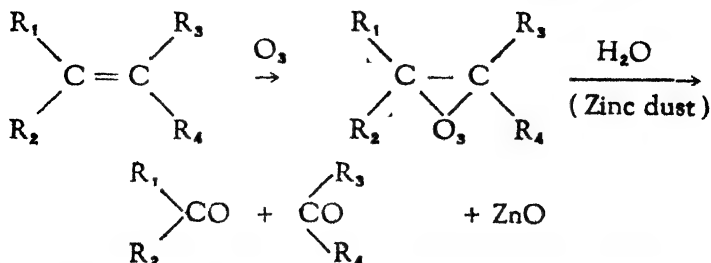
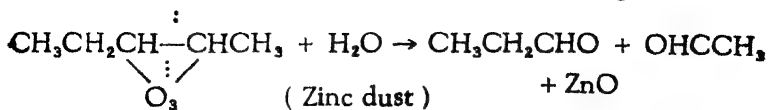
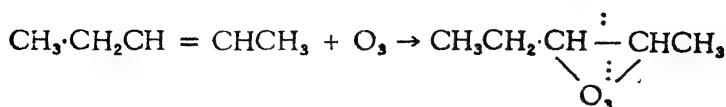
$$CH_3{\cdot}CH = CH_2 + H{\cdot}HSO_4 \rightarrow CH_3CH(HSO_4)CH_3$$

(vi) Ozone yields ozonide, which is hydrolysed by water giving aldehydes or ketones.

$$CH_3{\cdot}CH_2CH = CHCH_3 + O_3 \rightarrow CH_3CH_2{\cdot}CH \overset{:}{—} CHCH_3 \text{ (bridged by } O_3)$$

$$CH_3CH_2CH \overset{:}{—} CHCH_3 \text{ (bridged by } O_3) + H_2O \xrightarrow{\text{(Zinc dust)}} CH_3CH_2CHO + OHCCH_3 + ZnO$$

$$\begin{matrix} R_1 & & R_3 \\ & C = C & \\ R_2 & & R_4 \end{matrix} \xrightarrow{O_3} \begin{matrix} R_1 & & R_3 \\ & C - C & \\ R_2 & O_3 & R_4 \end{matrix} \xrightarrow[\text{(Zinc dust)}]{H_2O}$$

$$\begin{matrix} R_1 \\ R_2 \end{matrix}{>}CO + CO{<}\begin{matrix} R_3 \\ R_4 \end{matrix} + ZnO$$

(vii) Oxidation with potassium permanganate solution to polyalcohols, aldehydes, ketones, or acids depending upon the degree of oxidation.

(viii) Polymerisation.

III. Acetylenes

(*A*) *Preparation.* } They are the same as those of the
(*B*) *Properties.* } olefines.

IV. Aromatic Hydrocarbons

(*A*) *Preparation.* (i) From halogen compounds. (ii) Distillation of salt with soda lime (NaOH). (iii) Reduction of carbon monoxide —CO to CH_2 (Clemmensen Reduction). (iv) Replacement of $—SO_3H$ by H (heating at high temperatures with steam). (v) Diazotisation of primary amines and boiling with ethyl alcohol or sodium stannite. (vi) Distillation of phenols with zinc dust.

(*B*) *Properties.* (i) Substitution: (*a*) Halogenation. (*b*) Nitration. (*c*) Sulphonation. (ii) Addition: (*a*) Hydrogenation. Sabatier's method of using hydrogen with a catalyst (Ni) at high temperature, (*b*) Addition of halogen—Special conditions for preparation and relative unstable character of the product, (*c*) Addition of ozone. (iii) Oxidation: (*a*) General stability of aromatic nucleus towards aqueous oxidising agents, (*b*) Side chains are ultimately degraded to —COOH irrespective of their length or structure.

Particular examples of oxidation—

(1) Diphenylmethane to diphenylketone.

(2) Triphenylmethane to triphenylcarbinol.

(3) *o*–, *m*– or *p*–xylene to phthalic, isophthalic or terephthalic acids.

(4) Oxidation of benzene through benzoquinone to maleic acid by catalytic vapour phase method.

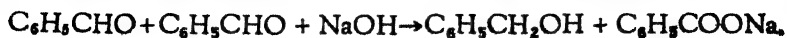
(5) Naphthalene to phthalic acid by the same method as in (4).

(6) Anthracene to anthraquinone.

(2) Hydroxy Compounds

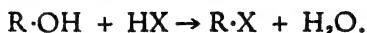
I. Alcohols.

(*A*) *Preparation*. (i) Hydrolysis of Esters. (ii) Action of sodium hydroxide on alkyl halides. (iii) Reduction of aldehydes and ketones. Aldehydes give primary alcohols while ketones give secondary ones. (iv) Dismutation (disproportionation) of aromatic aldehydes with concentrated alkali :

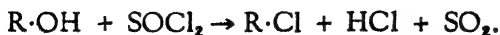
$$C_6H_5CHO + C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa.$$

(v) Action of nitrous acid on primary aliphatic amines. (vi) Oxidation of aromatic hydrocarbons containing H attached to a tertiary carbon atom *

$$(C_6H_5)_3\,CH \rightarrow (C_6H_5)_3COH.$$

(*B*) *Properties*. (i) Liberation of H by Na. (ii) Formation of ester with acids. (iii) Formation of ester with acid chlorides. (iv) Formation of ester with acid anhydrides. (v) Formation of alkyl halides with hydrogen halide.

$$R{\cdot}OH + HX \rightarrow R{\cdot}X + H_2O.$$

(vi) With inorganic acid halide yielding alkyl halide.

$$R{\cdot}OH + PCl_5 \rightarrow R{\cdot}Cl + POCl_3 + HCl.$$

$$R{\cdot}OH + SOCl_2 \rightarrow R{\cdot}Cl + HCl + SO_2.$$

(vii) Oxidation to aldehydes and ketones. Primary alcohols give aldehydes while secondary ones yield ketones. (viii) Dehydration of alcohols with H_2SO_4 and P_2O_5

(*a*) yielding ethers

$$2CH_3CH_2OH \rightarrow CH_3CH_2OCH_2CH_3 + H_2O,$$

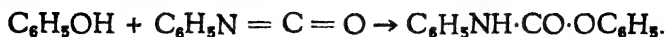
(*b*) yielding alkenes

$$CH_3CH_2CH_2OH \rightarrow CH_3CH : CH_2 + H_2O.$$

II. Phenols

(*A*) *Preparation*. (i) From sulphonic acid—fusion of salts with alkali followed by acidification. (ii) Action of nitrous acid on primary amines.

(*B*) *Properties.* (i) Acidic character—solubility in NaOH. (ii) Formation of phenol ethers on treatment with alkyl halide (or sulphate) usually in the presence of alkali. (iii) Formation of phenol esters on treatment with acyl halide in the presence of aqueous alkali (Schotten—Baumann Method) or pyridine (Einhorn Method). (iv) Formation of N–substituted carbamates by the action of isocyanate,

$$C_6H_5OH + C_6H_5N = C = O \rightarrow C_6H_5NH \cdot CO \cdot OC_6H_5.$$

(v) Replacement of OH by Cl by the action of phosphorus pentachloride. (vi) Reduction to hydrocarbon by heating with zinc dust. (vii) Catalytic hydrogenation. (viii) Substitution products such as tribromo phenol, sulphonic acid and nitro phenols. (ix) Nitrosation : formation of *p*–nitroso-phenol. (x) Coupling with diazonium salts. (xi) Condensation : (*a*) with phthalic anhydride yielding phthaleins—preparation of phenol-phthalein, (*b*) with aromatic aldehydes. (xii) Oxidation to quinones. (xiii) Di–and poly–hydric phenols are powerful reducing agents. (xiv) Colouration with ferric chloride ($FeCl_3$).

(3) Alcohol Derivatives

I. Alkyl Halides

(*A*) *Preparation.* (i) Direct substitution. (ii) Addition of HX to unsaturated linkage. (iii) Reaction of halogen hydride on alcohol,

$$ROH + HCl \rightarrow R \cdot Cl + H_2O.$$

(iv) Alcohol and inorganic acid halide,

$$3R \cdot OH + PCl_3 \rightarrow 3R \cdot Cl + P(OH)_3.$$

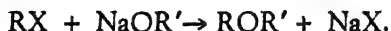
(*B*) *Properties.* (i) Replacement of halogen : (*a*) by OH,

$$RX + NaOH \rightarrow R \cdot OH + NaX.$$

(*b*) by NH_2 with NH_3, (*c*) by CN with KCN , (*d*) by H with hydrogen,

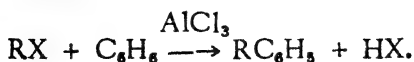
$$RX + 2H \rightarrow RH + HX.$$

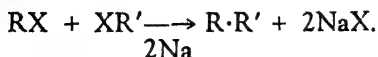
(ii) Formation of ether with alcoholate,

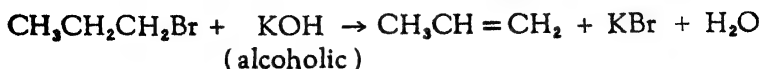
$$RX + NaOR' \rightarrow ROR' + NaX.$$

(iii) Formation of ester with sodium salt of an acid,

$$RX + NaOOCR' \rightarrow ROOCR' + NaX.$$

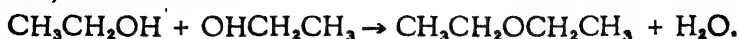
(iv) Friedel–Craft's Reaction,

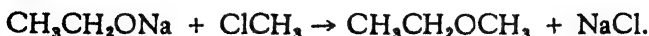
$$RX + C_6H_6 \xrightarrow{AlCl_3} RC_6H_5 + HX.$$

(v) Coupling of alkyl radicals (Wurtz's Reaction)

$$RX + XR' \xrightarrow[2Na]{} R{\cdot}R' + 2NaX.$$

(vi) Loss of HX with alcoholic caustic potash,

$$CH_3CH_2CH_2Br + \underset{(alcoholic)}{KOH} \rightarrow CH_3CH=CH_2 + KBr + H_2O$$

II. Ethers

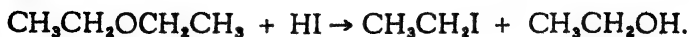
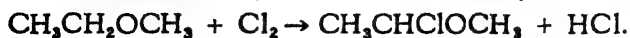
(A) *Preparation.* (i) Bimolecular dehydration of alcohols,

$$CH_3CH_2OH + OHCH_2CH_3 \rightarrow CH_3CH_2OCH_2CH_3 + H_2O.$$

(ii) Metal alcoholate and alkyl halide give ethers (Williamson),

$$CH_3CH_2ONa + ClCH_3 \rightarrow CH_3CH_2OCH_3 + NaCl.$$

(B) *Properties.* (i) Splitting with hydrogen iodide on heating,

$$CH_3CH_2OCH_2CH_3 + HI \rightarrow CH_3CH_2I + CH_3CH_2OH.$$

(ii) Substitution by chlorine or bromine,

$$CH_3CH_2OCH_3 + Cl_2 \rightarrow CH_3CHClOCH_3 + HCl.$$

(iii) Oxidation to peroxide.

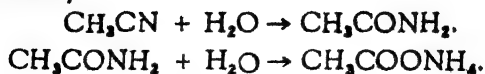
III. Nitriles

(A) *Preparation.* (i) KCN and alkyl halide,

$$KCN + CH_3Cl \rightarrow KCl + CH_3CN.$$

(B) *Properties.* (i) Hydrolysis upto acid via amide,

ammonium salt,

$$CH_3CN + H_2O \rightarrow CH_3CONH_2.$$
$$CH_3CONH_2 + H_2O \rightarrow CH_3COONH_4.$$

(4) Carbonyl Compounds

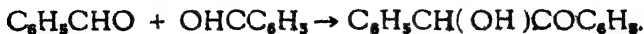
I. Aldehydes

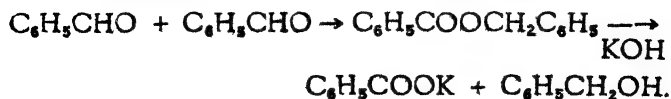
(*A*) *Preparation.* (i) Oxidation or dehydrogenation of primary alcohols. Oxidation may be effected by potassium dichromate and sulphuric acid or air and catalyst. Dehydrogenation is effected by passing vapours of alcohol over copper or silver at high temperature. (ii) Partial oxidation of aliphatic side chain. (iii) Hydrolysis of compounds containing $—CHCl_2$ group. (iv) Hydrolysis of ozonides. (v) Reduction of acid chlorides, anhydrides or esters. (vi) Heating the salt of an acid with a salt of formic acid.

(*B*) *Properties.* (i) Oxidation to acid with the same number of carbon atoms. (ii) Reduction to primary alcohols. (iii) Formation of additive compounds with ammonia, hydrocyanic acid, sodium bisulphite. (iv) Formation of hydrazones with hydrazines, and aldoximes with hydroxylamine. (v) PCl_5 replaces CO by CCl_2. (vi) Condensation. (vii) Polymerisation.

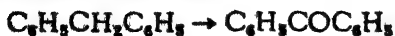
Aromatic aldehydes.

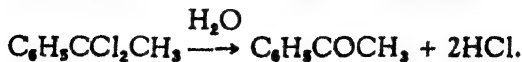
(viii) Benzoin condensation under the influence of dilute aqueous potassium cyanide,

$$C_6H_5CHO + OHCC_6H_5 \rightarrow C_6H_5CH(OH)COC_6H_5.$$

(ix) Cannizaro's reaction with strong alkali.

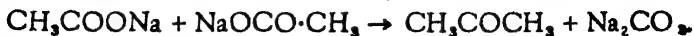
$$C_6H_5CHO + C_6H_5CHO \rightarrow C_6H_5COOCH_2C_6H_5 \xrightarrow{KOH} C_6H_5COOK + C_6H_5CH_2OH.$$

II. Ketones

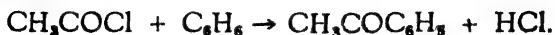
(*A*) *Preparation.* (i) Oxidation (or dehydrogenation with catalyst) of secondary alcohols. (ii) Oxidation of suitably constituted aromatic hydrocarbon,

$$C_6H_5CH_2C_6H_5 \rightarrow C_6H_5COC_6H_5$$

(iii) Hydrolysis of compounds containing $= CCl_2$ group

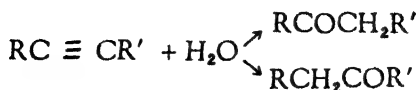
$$C_6H_5CCl_2CH_3 \xrightarrow{H_2O} C_6H_5COCH_3 + 2HCl.$$

(iv) Hydrolysis of ozonides.

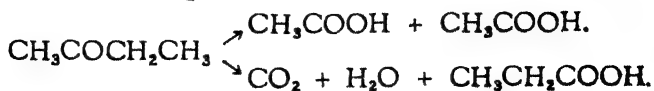
(v) Heating the salt of an acid,

$$CH_3COONa + NaOCO{\cdot}CH_3 \rightarrow CH_3COCH_3 + Na_2CO_3.$$

(vi) Friedel and Craft's reaction in the presence of aluminium chloride,

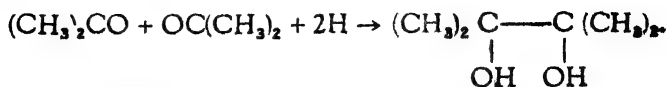
$$CH_3COCl + C_6H_6 \rightarrow CH_3COC_6H_5 + HCl.$$

(vii) Catalytic hydration of substituted acetylenes,

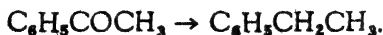
$$RC \equiv CH + H_2O \rightarrow RCO{\cdot}CH_3$$

$$RC \equiv CR' + H_2O \begin{array}{l} \nearrow RCOCH_2R' \\ \searrow RCH_2COR' \end{array}$$

(*B*) *Properties.* (i) Oxidation to acids containing fewer carbon atoms than the original Ketone.

$$CH_3COCH_2CH_3 \begin{array}{l} \nearrow CH_3COOH + CH_3COOH. \\ \searrow CO_2 + H_2O + CH_3CH_2COOH. \end{array}$$

(ii) Reduction to secondary alcohols.

(iii) Formation of pinacols.

$$(CH_3)_2CO + OC(CH_3)_2 + 2H \rightarrow (CH_3)_2\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}(CH_3)_2.$$

(iv) Clemmensen reduction with amalgamated zinc and hydrochloric acid to hydrocarbons,

$$C_6H_5COCH_3 \rightarrow C_6H_5CH_2CH_3.$$

(v) Additive product with sodium bisulphite. (vi) Formation of cyanohydrin with hydrogen cyanide. (vii) Formation of ketoximes with hydroxyl amine. (viii) Formation of hydrazones with hydrazine. (ix) Replacement of CO by CCl_2 by PCl_5.

$$(CH_3)_2CO + PCl_5 \rightarrow (CH_3)_2CCl_2 + POCl_3.$$

(x) Condensation.

III. Quinones

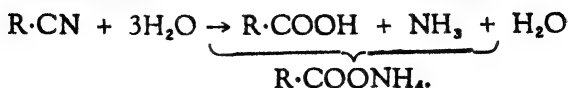
(*A*) *Preparation.* (i) Oxidation: (*a*) of mono hydroxy or monamino derivative of aromatic hydrocarbons *i. e.* phenols or amines, (*b*) of dihydroxy or diamino derivatives of hydrocarbons, (*c*) of aminophenols.

(*B*) *Properties.* (i) Oxidising action—liberation of iodine from faintly acid potassium iodide solution. (ii) Ketonic action of CO group. (iii) Addition reactions: (*a*) of halogens—chlorine or bromine, (*b*) of halogen hydride (hydrochloric acid, hydrobromic acid) yielding 2–chloro or 2–bromo hydroquinones, (*c*) of nascent hydrogen cyanide yielding 3 : 6 dihydroxy phthalonitrile. (iv) Substitution products—chlorine or bromine.

(5) Acids and Acid Derivatives

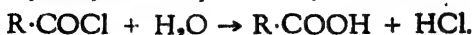
I. Acids

(*A*) *Preparation.* (i) Hydrolysis of nitriles,

$$R{\cdot}CN + 3H_2O \rightarrow \underbrace{R{\cdot}COOH + NH_3}_{R{\cdot}COONH_4} + H_2O$$

(ii) Hydrolysis of esters,

$$R{\cdot}CO{\cdot}OR_1 + H_2O \rightarrow R{\cdot}COOH + R_1OH.$$

(iii) Hydrolysis of acyl halides,

$$R{\cdot}COCl + H_2O \rightarrow R{\cdot}COOH + HCl.$$

(iv) Action of Nitrous acid on amides,

$$R{\cdot}CONH_2 + HNO_2 \rightarrow R{\cdot}COOH + N_2 + H_2O.$$

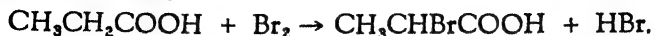
(v) Hydrolysis of —CCl_3 group,

$$R{\cdot}CCl_3 + 3H_2O \rightarrow R{\cdot}COOH + 3HCl + H_2O.$$

(vi) Oxidation of aldehydes. (vii) Oxidation of ketones. (viii) Oxidation of unsaturated carbon linkage. (ix) Oxidation of side chains attached to aromatic nuclei,

$$C_6H_5CH_3 \rightarrow C_6H_5COOH + H_2O.$$

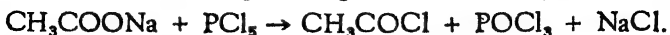
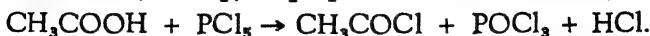
(*B*) *Properties.* (i) Salt formation with metals or metallic oxides and hydroxides. (ii) Esterification with alcohols. (iii) Replacement of OH by Cl by the action of phosphorus penta- or trichloride, or of thionyl chloride ($SOCl_2$). (iv) Formation of hydrocarbon on heating with soda lime. (v) Formation of aldehyde on heating the salt of the acid with that of formic acid. (vi) Formation of ketones on heating the salt of the acid. (vii) Substitution by halogen of hydrogen atoms (Hell-Volhardt-Zelinsky Reaction).

$$CH_3CH_2COOH + Br_2 \rightarrow CH_3CHBrCOOH + HBr.$$

There are no special methods of *preparation* and no special *properties* of AROMATIC ACIDS.

II. ACYL HALIDES

(*A*) *Preparation.* (i) The action of phosphorus pentachloride, trichloride, $SOCl_2$, SO_2Cl_2 on free acid or its salt,

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl.$$

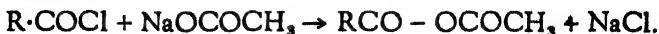
$$CH_3COONa + PCl_5 \rightarrow CH_3COCl + POCl_3 + NaCl.$$

(*B*) *Properties.* (i) Hydrolysis yielding free acid,

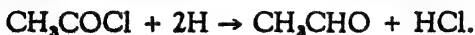
$$R{\cdot}COCl + H_2O \rightarrow R{\cdot}COOH + HCl.$$

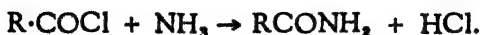
(ii) Alcohol, alcoholate, phenol and phenolates yield esters,

$$R{\cdot}COCl + NaOC_6H_5 \rightarrow R{\cdot}COOC_6H_5 + NaCl.$$

(iii) Salts of the acid give anhydride,

$$R{\cdot}COCl + NaOCOCH_3 \rightarrow RCO - OCOCH_3 + NaCl.$$

(iv) Nascent hydrogen reduces to aldehyde,

$$CH_3COCl + 2H \rightarrow CH_3CHO + HCl.$$

(v) Ammonia, primary amines and secondary amines yield amides (or substituted amides).

$$R{\cdot}COCl + NH_3 \rightarrow RCONH_2 + HCl.$$

III. ANHYDRIDE

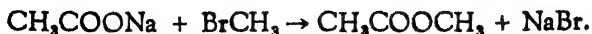
(*A*) *Preparation.* (i) Acyl chloride and salt of the acid.

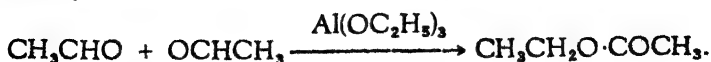
$$R{\cdot}COCl + NaCOOR \rightarrow RCO - O - COR + NaCl.$$

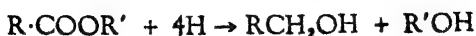
(*B*) *Properties.* They are practically the same as those of acyl halide.

IV. Esters

(*A*) *Preparation.* (i) Acid + Alcohol. (ii) Acyl halide + Alcohol (or alcoholate). (iii) Salt of acid + alkyl halide,

$$CH_3COONa + BrCH_3 \rightarrow CH_3COOCH_3 + NaBr.$$

(iv) Catalytic condensation of aldehydes. (Tischtschenko Reaction),

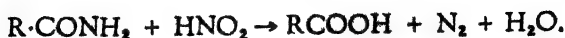
$$CH_3CHO + OCHCH_3 \xrightarrow{Al(OC_2H_5)_3} CH_3CH_2O\cdot COCH_3.$$

(*B*) *Properties.* (i) Hydrolysis with water. (ii) Splitting with hydroiodic or sulphuric acid. (iii) Ammonia, amines yield amides or substituted amides. (iv) Nascent hydrogen (Borocault-Blare Reaction) or hydrogen with catalyst reduces to alcohol.

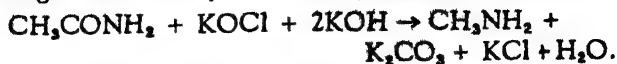
$$R\cdot COOR' + 4H \rightarrow RCH_2OH + R'OH$$

V. Amides

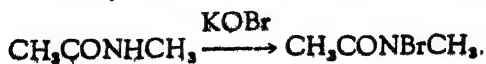
(*A*) *Preparation.* (i) Dehydration of ammonium salts (ii) Acid derivative (halides, anhydrides, esters) with ammonia amines yield amides. (iii) Nitrile and water.

$$CH_3C \equiv N + H_2O \rightarrow CH_3CONH_2.$$

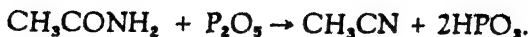
(*B*) *Properties.* (i) Hydrolysis with water. (ii) Nitrous acid yields acid.

$$R\cdot CONH_2 + HNO_2 \rightarrow RCOOH + N_2 + H_2O.$$

(iii) Halogen and alkali yield amines (Hoffmann's Reaction).

$$CH_3CONH_2 + KOCl + 2KOH \rightarrow CH_3NH_2 + K_2CO_3 + KCl + H_2O.$$

Note :— N-alkyl amides yield only halogen compounds.

$$CH_3CONHCH_3 \xrightarrow{KOBr} CH_3CONBrCH_3.$$

(iv) Strong dehydrating agents (P_2O_5, PCl_5, etc.) yield

nitriles,

$$CH_3CONH_2 + P_2O_5 \rightarrow CH_3CN + 2HPO_3.$$

Note :— N-substituted amides cannot lose water to yield nitrile.

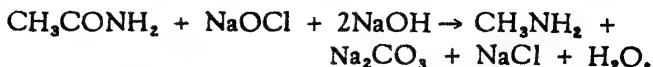
(6) Amines

I. Alkyl Amines

(*A*) *Preparation*. (i) Heating alkyl halides with ammonia.

$$CH_3Cl + NH_3 \rightarrow CH_3NH_2 + HCl.$$

(ii) Hofmann's Reaction.

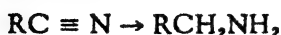
$$CH_3CONH_2 + NaOCl + 2NaOH \rightarrow CH_3NH_2 + Na_2CO_3 + NaCl + H_2O.$$

(iii) Reduction of nitriles, oximes, hydrazones, nitroso and nitro compounds.

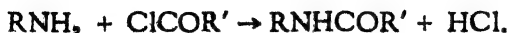
$$RC \equiv N \rightarrow RCH_2NH_2$$

$$RCNOH \rightarrow RCH_2NH_2$$

$$RCN : NH_2 \rightarrow RCH_2NH_2 + NH_3$$

$$RNO \rightarrow RNH_2 + H_2O$$

$$RNO_2 \rightarrow RNH_2 + 2H_2O$$

(*B*) *Properties*. (i) Formation of salt. (ii) Action of nitrous acid : (*a*) Primary amines yield alcohol, (*b*) Secondary amines yield liquid or solid nitroso amine, (*c*) No action on tertiary amines, (iii) Acyl halides, anhydrides and esters yield amides.

$$RNH_2 + ClCOR' \rightarrow RNHCOR' + HCl.$$

II. Aromatic Amines—Primary Amines

(*A*) *Preparation*. (i) Reduction of nitro, nitroso or azo, also of nitriles, oximes, hydrazones, etc. as in aliphatic amines. (ii) Amidation (*a*) from aryl halides by treatment of ammonia (liquid or under pressure with catalyst); (*b*) from phenols (naphthols) by heating with zinc chloride and ammonia. (iii) Hofmann's degradation of amides. (iv) Rearrangement : (*a*) Acid rearrangement of hydrazo compounds to diamino biphenyl derivative. (*b*) Acid rearrangement of hydroxylamines to

aminophenols. (*c*) Rearrangement of secondary amines to primary amines.

(*B*) *Properties.* (i) Acylation—use of acyl halide (or anhydride) aqueous alkali (Schotten–Baumann) or pyridine (Einhorn) facilitates the reaction. (ii) Alkylation. (iii) Formation of salts with acids. (iv) Nitrous acid yields phenols [Primary amines]. (v) Catalytic hydrogenation reduces aniline to cyclo hexylamine—loss of aromatic character. (vi) Substitution in benzene ring : (*a*) Halogenation. (*b*) Sulphonation. (*c*) Nitration. (vii) Coupling with diazonium salt. (viii) Oxidation to quinones.

III. Aromatic Amines—Secondary Amines

(*A*) *Preparation.* (i) Alkylation of primary amines

(*B*) *Properties.* (i) Nitrous acid yields N–nitrosoamine—rearrangement (with acid) to *p*—nitroso (primary) amines, acid reduction of the latter to N–alkyl–*p*–diamines—acid reduction of N–nitrosoamines to asymmetrical hydrazines ($R_2N \cdot NH_2$). (ii) Arylsulphonyl chloride yields N–sulphonyl amines (insoluble in aqueous alkali). (iii) Action of heat—rearrangement of N–methylamine to *p*–toluidine.

IV. Aromatic Amines—Tertiary Amines

(*A*) *Preparation.* (i) Alkylation of primary (or secondary) amines.

(*B*) *Properties.* (i) Nitrous acid yields *p*–nitroso derivative. (ii) Coupling with diazonium salt. (iii) Formation of quaternary ammonium salts.

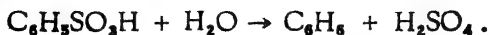
(7) Aromatic Derivatives

I. Sulphonic Acid

(*A*) *Preparation.* (i) Direct sulphonation.

(*B*) *Properties.* (i) Phosphorus pentachloride yields sulphonyl chloride which forms esters with alcohol or phenol. (ii) Alcohol yields esters. (iii) Fusion with alkali yields

phenols. (iv) Alkali cyanide gives nitriles. (v) Superheated steam gives hydrocarbon.

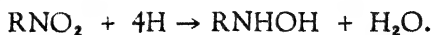
$$C_6H_5SO_3H + H_2O \rightarrow C_6H_6 + H_2SO_4.$$

II. Nitro Compounds.

(*A*) *Preparation.* (i) Direct nitration.

(*B*) *Properties.* (i) Reduction: (*a*) Acid solution $SnCl_2$ + HCl, $TiCl_3$ + HCl, etc.) reduces to amines.

$$RNO_2 \xrightarrow{6H} RNH_2 + 2H_2O.$$

(b) Neutral solution (zinc + aqueous alcohol, zinc + NH_4Cl, etc.) reduction to hydroxyl amine derivatives.

$$RNO_2 + 4H \rightarrow RNHOH + H_2O.$$

(*c*) Alkali solution – (zinc dust + aqueous alkali) yield

(1) RNO = NR′ azoxy compound.

(2) RN : NR′ azo compounds.

(3) RNH : NHR′ Hydrazo compounds which disproportionate on heating,

$$2C_6H_5NH : NHC_6H_5 \rightarrow C_6H_5N : NC_6H_5 + 2C_6H_5NH_2.$$

III. Halogen Compounds

(A) *Preparation.* (i) Direct halogenation (ii) Diazotization and subsequent reaction of diazonium salt with CuCl, CuBr, and KI. (iii) Replacement of OH in phenols by Cl with PCl_5.

(B) *Properties.* (i) Generally inert, (ii) Substitution in the ring, (iii) Friedel–Craft's Reaction.

(8) Special Reactions

I. Diazo Compounds and Diazonium Salts

(*A*) *Preparation.* (i) Addition of the required amount of nitrous acid to primary amine in acid solution at a very low

temperature. (ii) The isolation of diazonium salt may be effected by using non-aqueous solutions.

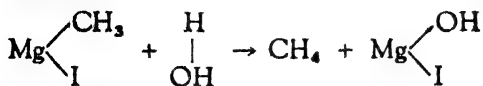
(B) *Properties.* Replacement of (i) —N —NX by OH (Phenols) by warming with water (ii) —NNX by OR (phenol ethers) by warming with alcohols (iii) —NNX by H by warming with alcohol which is dehydrogenated to aldehyde (iv) —NNX by H by treatment with alkaline $SnCl_2$ (Na_2SnO_2) (v) —NNX by —Cl —Br, —I or —CN, (*a*) Sandmeyer's Reaction: use of CuCl,CuBr or CuCN (*b*) Gattermann's Reaction: use of catalytic copper, (*c*) by I, no catalyst, merely KI. (vi) Reduction to aryl hydrazine in acid solution ($SnCl_2$ + HCl, Na_2SO_3, zinc dust + acetic acid). (vii) Coupling with phenols and amines.

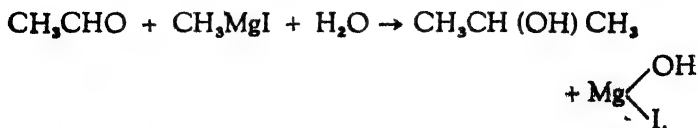
II. Grignard's reagent

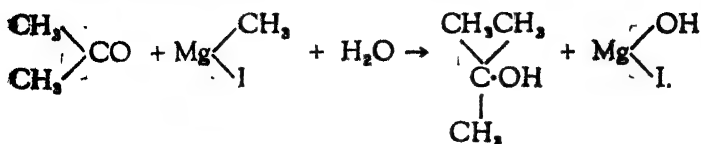
$$Mg\begin{smallmatrix} R \\ X \end{smallmatrix}$$

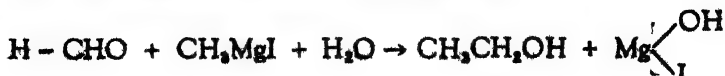
General formula of the reagent where R is alkyl or aryl radical and X the halogen.

Reactions. (i) Water yields a hydrocarbon

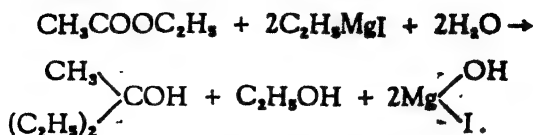
$$Mg\begin{smallmatrix} CH_3 \\ I \end{smallmatrix} + \begin{smallmatrix} H \\ | \\ OH \end{smallmatrix} \rightarrow CH_4 + Mg\begin{smallmatrix} OH \\ I \end{smallmatrix}$$

(ii) With aldehyde secondary alcohols are formed,

$$CH_3CHO + CH_3MgI + H_2O \rightarrow CH_3CH(OH)CH_3 + Mg\begin{smallmatrix} OH \\ I. \end{smallmatrix}$$

(iii) Ketones give tertiary alcohols,

$$\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}CO + Mg\begin{smallmatrix} CH_3 \\ I \end{smallmatrix} + H_2O \rightarrow \begin{smallmatrix} CH_3CH_3 \\ \diagdown\diagup \\ C\cdot OH \\ | \\ CH_3 \end{smallmatrix} + Mg\begin{smallmatrix} OH \\ I. \end{smallmatrix}$$

(iv) Formaldehyde yields primary alcohol

$$H-CHO + CH_3MgI + H_2O \rightarrow CH_3CH_2OH + Mg\begin{smallmatrix} OH \\ I \end{smallmatrix}$$

(v) Esters give tertiary alcohol

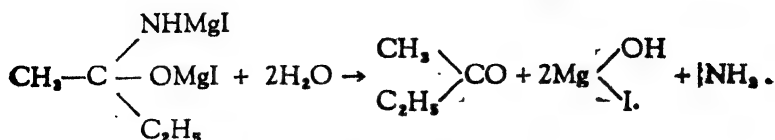
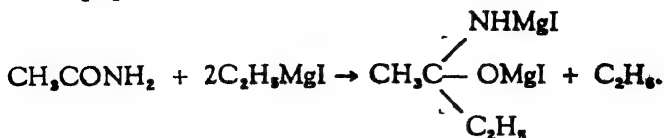
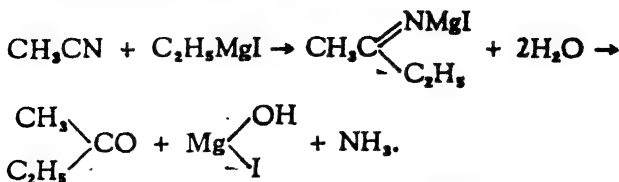
$$CH_3COOC_2H_5 + 2C_2H_5MgI + 2H_2O \rightarrow$$

$$\begin{matrix} CH_3 \\ (C_2H_5)_2 \end{matrix} \!\!> COH + C_2H_5OH + 2Mg \!<\! \begin{matrix} OH \\ I \end{matrix}.$$

(vi) Cyanides and amides yield ketones.

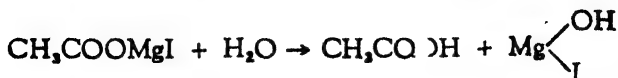
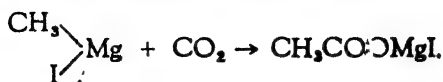
$$CH_3CN + C_2H_5MgI \rightarrow CH_3C \!<\! \begin{matrix} {=}NMgI \\ C_2H_5 \end{matrix} + 2H_2O \rightarrow$$

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \!\!> CO + Mg \!<\! \begin{matrix} OH \\ I \end{matrix} + NH_3.$$

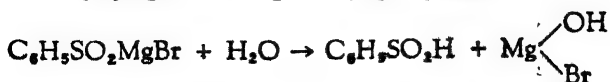
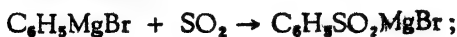
$$CH_3CONH_2 + 2C_2H_5MgI \rightarrow CH_3C \!\begin{matrix} / NHMgI \\ - OMgI \\ \backslash C_2H_5 \end{matrix} + C_2H_6.$$

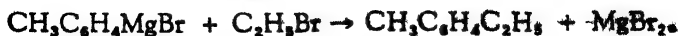
$$CH_3{-}C \!\begin{matrix} / NHMgI \\ - OMgI \\ \backslash C_2H_5 \end{matrix} + 2H_2O \rightarrow \begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \!\!> CO + 2Mg \!<\! \begin{matrix} OH \\ I. \end{matrix} + NH_3.$$

(vii) Carbon dioxide yields an acid.

$$\begin{matrix} CH_3 \\ I \end{matrix} \!\!> Mg + CO_2 \rightarrow CH_3COOMgI.$$

$$CH_3COOMgI + H_2O \rightarrow CH_3COOH + Mg \!<\! \begin{matrix} OH \\ I \end{matrix}$$

(viii) With sulphur dioxide, sulphinic acid is formed.

$$C_6H_5MgBr + SO_2 \rightarrow C_6H_5SO_2MgBr;$$

$$C_6H_5SO_2MgBr + H_2O \rightarrow C_6H_5SO_2H + Mg \!<\! \begin{matrix} OH \\ Br \end{matrix}$$

(ix) Alkyl halides give hydrocarbons.

$$CH_3C_6H_4MgBr + C_2H_5Br \rightarrow CH_3C_6H_4C_2H_5 + MgBr_2.$$

III. The Friedel–Craft Reaction

By the use of anhydrous aluminium chloride as catalyst, a large number of condensations can be effected.

(i) Hydrocarbon.

$$C_6H_6 + CH_3Cl \xrightarrow[AlCl_3]{} C_6H_5CH_3 + HCl.$$

(ii) Aldehydes.

(*a*) $C_6H_5CH_3 + HCl + CO \rightarrow C_6H_4\begin{cases}CH_3\\CHO\end{cases} + HCl.$

(*b*) $C_6H_5OCH_3 + \underset{(HCl\ +\ HCN)}{ClCH{\cdot}NH} \rightarrow C_6H_4\begin{cases}OCH_3\\CH:NH\end{cases} + HCl.$

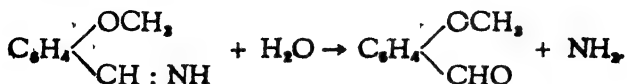
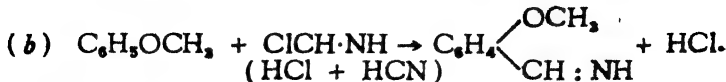
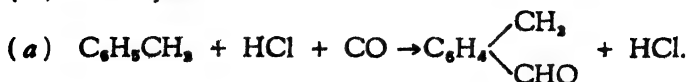
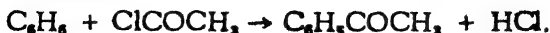
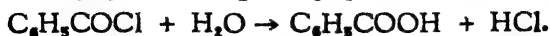
$$C_6H_4\begin{cases}OCH_3\\CH:NH\end{cases} + H_2O \rightarrow C_6H_4\begin{cases}OCH_3\\CHO\end{cases} + NH_3.$$

(iii) Ketone.

$$C_6H_6 + ClCOCH_3 \rightarrow C_6H_5COCH_3 + HCl.$$

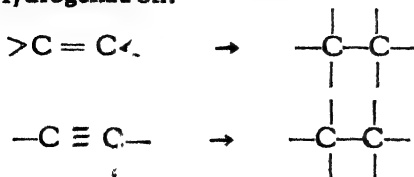
(iv) Acid.

$$C_6H_6 + COCl_2 \rightarrow C_6H_5COCl + HCl.$$

$$C_6H_5COCl + H_2O \rightarrow C_6H_5COOH + HCl.$$

(9) Reduction

(1) Hydrogenation.

$$>C=C< \quad \rightarrow \quad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

$$-C\equiv C- \quad \rightarrow \quad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

(2) Carbonyl → Carbinol.

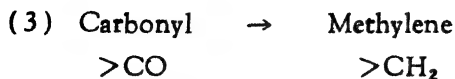
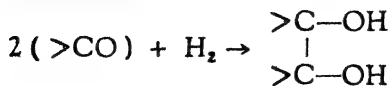
$>CO \qquad >CHOH.$

(*a*) Use of sodium amalgam (for ketones only) (*b*) Sodium and acetic acid (*c*) Zinc dust and acetic acid (*d*) aluminium ethoxide (*e*) Sabatier—Senderen's process of hydrogenation over reduced nickel at 100° and 165°.

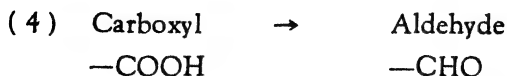
Note:—The reduction of carbonyl sometimes leads to pinacone.

$$2(>CO) + H_2 \rightarrow \begin{array}{l} >C-OH \\ \quad | \\ >C-OH \end{array}$$

(3) Carbonyl → Methylene

$>CO$ $>CH_2$

(*a*) Sodium + (hot) ethyl or amyl alcohol, (*b*) Clemmensen's Method: amalgamated zinc and hydrochloric acid, (*c*) Heating the semicarbazone or hydrazone of the carbonyl compound with sodium ethoxide at 170° – 180°.

(4) Carboxyl → Aldehyde

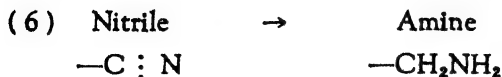
$-COOH$ $-CHO$

(*a*) Sodium amalgam or zinc and acid, (*b*) Passing vaporised acid mixed with formic acid over TiO_2 at 250° – 300°, (*c*) Hydrogenating acid chloride in presence of palladised barium sulphate or kisselguhr.

(5) Carboxyl → Carbinol

$-COOH$ $-CH_2OH$

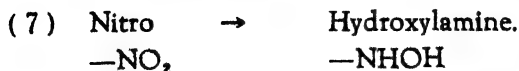
(*a*) Sodium amalgam or zinc and acid, (*b*) Electro reduction, (*c*) Reduction of ester by means of sodium and ethyl or amyl alcohol (Bonveault–Blanc), (*d*) Catalytic reduction.

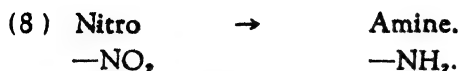
(6) Nitrile → Amine

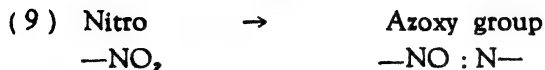
$-C \vdots N$ $-CH_2NH_2$

(*a*) Action of sodium on alcoholic solution of nitrile.

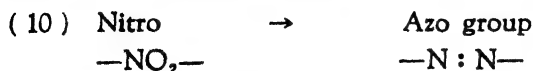
Note:—Sabatier–Senderens' Method gives secondary amines.

(7) Nitro → Hydroxylamine.

$-NO_2$ $-NHOH$

(*a*) $SnCl_2 + HCl$, (*b*) Electro reduction of alcoholic solution + H_2SO_4, (*c*) Zinc dust and aqueous ammonium chloride.

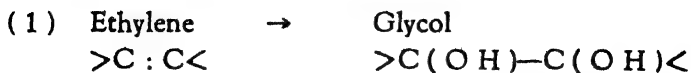
(8) Nitro → Amine.
—NO_2 —NH_2.

(*a*) Sn + HCl, (*b*) $SnCl_2$ + HCl, (*c*) Zn + HCl, (*d*) Fe + HCl (or acetic acid), (*e*) Alkali sulphide also ammonium sulphide, (*f*) Titanous chloride, (*g*) Zinc dust in boiling aqueous alcohol containing ammonium chloride.

(9) Nitro → Azoxy group
—NO_2 —NO : N—

(*a*) Boiling alcoholic potash (or sodium methoxide), (*b*) Magnesium amalgam and alcohol, (*c*) Calcium and alcohol, (*d*) Sodium amalgam and alcohol, (*e*) Zinc dust and alcoholic ammonia, (*f*) Sodium Arsenite.

(10) Nitro → Azo group
—NO_2— —N : N—

(*a*) Alkaline Stannite, (*b*) Zinc dust and alkali in the presence of alcohol.

Note:— These methods can also be used for preparing hydrazo group.

(10) Oxidation

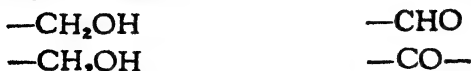
(1) Ethylene → Glycol
>C : C< >C (O H)—C (O H)<

(*a*) Cold dilute solution of potassium permanganate, (*b*) Hydrogen peroxide in glacial acetic acid, (*c*) Saturated solution of mercuric acetate, (*d*) Lead tetra acetate, (*e*) Aqueous solution of sodium chlorate with osmium tetroxide as catalyst, (*f*) Organic per acids.

(2) Side chain → Carbonyl, >CO, —CHO.

(*a*) Manganese dioxide and sulphuric acid, (*b*) Chromyl chloride.

(3) Side chain → Carboxyl (—COOH)

(*a*) Alkaline permanganate, (*b*) Chromic acid.

(4) Hydroxy group → Aldehyde (or Ketone) group.

$—CH_2OH$ —CHO

$—CH_2OH$ —CO—

(*a*) Potassium dichromate and sulphuric acid, (*b*) Manganese dioxide and sulphuric acid, (*c*) Dehydrogenation with catalysts like copper, zinc, cadmium, platinum, silver, copper-silver, zinc-copper.

(5) Hydroxy → Carboxyl

$—CH_2OH$ —COOH

(*a*) Alkaline permanganate, (*b*) Heating with caustic soda or potash in autoclave at 250° to 270°.

(6) Carbonyl (aldehyde) → Carboxyl

—CHO —COOH.

(*a*) Permanganate, (*b*) Hydrogen peroxide, (*c*) Peracids. (*d*) Silver oxide, (*e*) Nitric acid, (*f*) Hypochlorite, (*g*) Oxygen.

(7) Amine → Nitroso

$—NH_2$ —NO

(*a*) Hydrogen peroxide, (tertiary amines only), (*b*) Caro's acid, (*c*) Peracetic acid, (*d*) Aqueous sodium peroxide, (*e*) Acidified ammonium persulphate with a little silver nitrate as catalyst.

Note :— Further oxidation of nitroso compounds yields nitro compounds.

(8) Amine → Azo.

(*a*) Lead peroxide and acetic acid.

(9) Amine → Quinone

(*a*) Chromic acid.

CHAPTER II

PROBLEMS WITH SOLUTIONS

(Selected mostly from various University-Examination Papers).

(1) An organic acid gave the following results on analysis. (i) 0·166 gm. yielded on combustion 0·352 gm. carbon dioxide and 0·054 gm. water; (ii) 0·285 gm. of the silver salt gave a residue which weighed 0·162 gm.; (iii) on heating, the acid lost water to the extent of 10·85% of its weight. Assign a structural formula to the acid.

The empirical formula:

		Per cent.	gm.atom	atomic ratio	
C	$= \dfrac{0{\cdot}352 \times 12 \times 100}{44 \times 0{\cdot}166} =$	57·83	4·82	2	4
H	$= \dfrac{0{\cdot}054 \times 2 \times 100}{18 \times 0{\cdot}166} =$	3·61	3·61	1·5	3
O	by difference $=$	38·56	2·41	1	2.

∴ The empirical formula is $C_4H_3O_2$.

The equivalent weight:

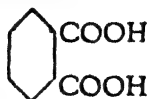
$$\frac{0{\cdot}285 \times 108}{0{\cdot}162} = 190 \quad \text{silver salt} - 108 + 1$$

$$= 83, \quad \text{equivalent weight.}$$

The molecular weight from the loss of water on the assumption that one molecule of water is given up :

$$\frac{100 \times 18}{10{\cdot}85} = 165{\cdot}9.$$

The acid is, therefore, a diabasic acid and its molecular formula is $C_8H_6O_4$. The two COOH groups are attached to C_6H_4.

The acid is, therefore,

Phthalic acid.

(2) A halogen derivative of an organic acid contained carbon = 17·26 per cent. and hydrogen = 2·16 per cent. 0·278 gm. of the acid gives 0·376 gm. AgBr, and 0·139 gm. of the acid requires 10 c.c. of $\frac{N}{10}$ caustic alkali for neutralisation. Suggest a formula for the acid.

To find the empirical formula :

		Per cent.	gm.atom	atomic ratio
C		= 17·26	1·44	2
H		= 2·16	2·16	3
Br	$= \frac{80 \times 0{\cdot}376 \times 100}{188 \times 0{\cdot}278}$	= 57·81	0·72	1
O	by difference	= 22·77	1·42	2

∴ The empirical formula of the acid is $C_2H_3O_2Br$.

$$\text{The equivalent weight of the acid} = \frac{0{\cdot}139 \times 10000}{10} = 139.$$

This equivalent weight agrees well with the empirical formula $C_2H_3O_2Br$ (= 139). The molecular formula of the acid therefore is the same as the empirical one. It is a mono bromo derivative of a monobasic acid which can be written as $CH_2BrCOOH$.

The acid is mono bromo acetic acid.

(3) 0·138 gm. of an aromatic hydrocarbon (A) gave on combustion 0·462 gm. of CO_2 and 0·108 gm. H_2O. The compound (A) on heating with dilute nitric acid in a sealed tube, gave a monobasic acid (B). 0·183 gm. of this acid required 30 c.c. of 0·05 N alkali for its complete neutralisation. When the

calcium salt of the above acid is distilled with slaked lime, another hydrocarbon (C) is obtained whose vapour density is found to be 39 (Density of H_2 taken as unity). What are the compounds (A), (B) and (C)?

Begin with (C):

The molecular weight of (C) = 39 × 2 = 78.

As it is an aromatic hydrocarbon it must contain at least 6 carbon atoms and 6 hydrogen atoms. The lowest member of these hydrocarbons is C_6H_6 with a molecular weight of 78 which is exactly the same as that of (C). (C) is therefore C_6H_6 benzene.

$$\text{The equivalent weight of (B)} = \frac{0{\cdot}183 \times 1000}{30 \times 0{\cdot}05} = 122.$$

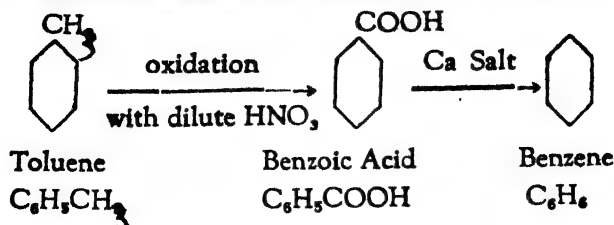
As it is a monobasic acid and as (C) is derived from it, it must contain an aromatic ring (78) and a COOH (45) group. An acid with a formula C_6H_5COOH has the same equivalent weight as found above. The acid (B) is, therefore, benzoic acid.

The hydrocarbon (A):

As the benzoic acid is formed by the oxidation of the hydrocarbon (A), (A) must contain at least 7 carbon atoms. The empirical formula of the hydrocarbon (A), is:

		Per cent.	gm. atom	atomic ratio
C	$= \frac{0{\cdot}462 \times 12 \times 100}{44 \times 0{\cdot}138}$	= 91·20	7·6	7
H	$= \frac{0{\cdot}108 \times 2 \times 100}{18 \times 0{\cdot}138}$	= 8·70	8·7	8

The empirical formula of (A) is C_7H_8. The molecular formula is the same as it contains 7 carbon atoms as required by the monobasic acid (B). The hydrocarbon (A) is, therefore, $C_6H_5CH_3$, *i. e.* Toluene.

The various reactions can be represented as follows :—

(4) 0·1935 gm. of an organic acid gave on combustion 0·132 gm. carbon dioxide and 0·0270 gm. water. 0·123 gm. of the same substance, when treated by Carius method for the estimation of halogen, gave 0·273 gm. of silver chloride. 0·645 gm. of the same substance required 61 c. c. of 0·082N NaOH. What is the acid ? Write the structural formula.

To calculate the empirical formula of the acid :

		Per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}132 \times 12 \times 100}{44 \times 0{\cdot}1935} =$	18·60	1·55	1
H	$= \frac{0{\cdot}0270 \times 100 \times 2}{18 \times 0{\cdot}1935} =$	1·51	1·51	1
Cl	$= \frac{0{\cdot}2736 \times 35{\cdot}5 \times 100}{0{\cdot}123 \times 143{\cdot}5} =$	54·33	1·55	1
O	by difference =	25·56	1·59	1

The empirical formula of the acid is CHOCl (64·5).

The equivalent weight of the acid $= \frac{0{\cdot}645 \times 1000}{61 \times 0{\cdot}082} = 128.$

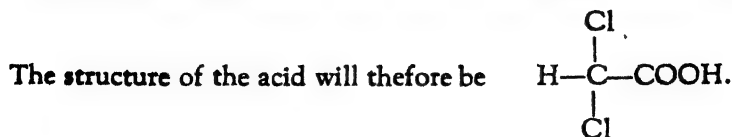
The molecular formula of the acid is, therefore, twice the empirical one.

It is $C_2H_2O_2Cl_2$ (129)

As the substance is a monobasic acid, its formula must contain —COOH group, and remaining hydrogen atom and

2 chlorine atoms must be attached to the other carbon atom.

The structure of the acid will thefore be

$$H-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-COOH.$$

The acid is dichloracetic acid.

(5) An aromatic nitro-compound (A) containing C = 58·5%, H = 4·1%, O = 26·0% , N = 11·4% gave on reduction with zinc dust in the alkaline solution, a compound (B) which, when boiled with concentrated hydrochloric acid, underwent an intramolecular change to a primary aromatic diamine (C). 0·41 gm. of the chloroplatinate of (C) with the formula $[(C)H_2PtCl_6]$ gave 0·134 gm. platinum on ignition. Assign structures to (A), (B) and (C) and write a short note on the reduction of (A).

The empirical formula of (A) :

	Per cent.	gm. atom	atomic ratio
C =	58·5	4·875	6
H =	4·1	4·1	5
O =	26·0	1·625	2
N =	11·4	0·811	1

The empirical formula of the nitro compound is $C_6H_5O_2N$.

The molecular weight of the chloroplatinate $[(C)H_2PtCl_6]$

$$= \frac{0{\cdot}41 \times 195}{0{\cdot}134} = 596{\cdot}6.$$

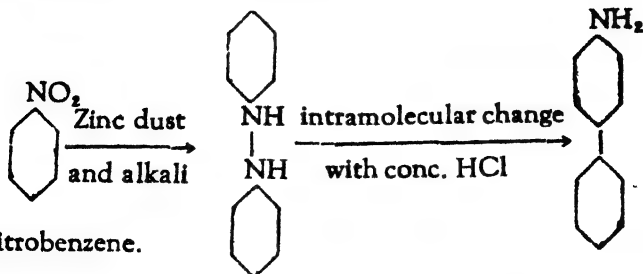
The molecular weight of H_2PtCl_6 = 410. Therefore, the molecular weight of the diamine,

$$= 596{\cdot}6 - 410 = 186{\cdot}6.$$

As the diamine is formed by an intramolecular change in an aromatic compound, it (the diamine, must contain two benzene rings and two amino groups. The simplest formula of the diamine would be di–amino–diphenyl.

$H_2N\langle\quad\rangle-\langle\quad\rangle NH_2$ having a molecular weight 184 which is fairly in agreement with the one found above (186·6).

The reactions can be represented as :

NO$_2$ — Zinc dust and alkali → NH—NH (intramolecular change with conc. HCl) → NH$_2$ … NH$_2$

(A) Nitrobenzene.

The same as the empirical formula.

(B) Hydrazobenzene

(C) *pp'* diamino-diphenyl Benzidine·

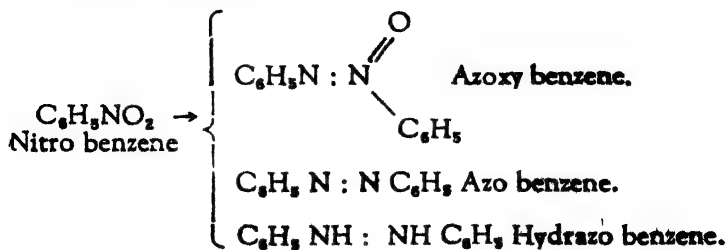
The reduction of nitro compounds in acid solution leads to the aromatic amines; the use of alkaline reducing agents such as sodium amalgam, zinc dust and caustic soda, and also potash and alcohol, gives rise to intermediate products, the azoxy, azo, hydrazo compounds, reduction in neutral solution yields phenyl-hydroxyl amine.

I Acid solution.

$$C_6H_5NO_2 \rightarrow C_6H_5NH_2$$

II Alkaline solution.

$C_6H_5NO_2 \rightarrow$ (Nitro benzene)

- $C_6H_5N : N(=O)C_6H_5$ Azoxy benzene.
- C_6H_5 N : N C_6H_5 Azo benzene.
- C_6H_5 NH : NH C_6H_5 Hydrazo benzene.

III Neutral Solution.

$$C_6H_5NO_2 \rightarrow C_6H_5NHOH$$

(6) 0·17 gm. of a monobasic organic acid gave on analysis 0·25 gm. of carbon dioxide and 0·103 gm. of water. 0·13 gm. of the acid neutralised 21/7 c. c. of N alkali. Deduce the formula of the acid.

The empirical formula of the acid :

			Per cent.	gm.atom	atomic ratio
C	=	$\frac{0{\cdot}25 \times 12 \times 100}{44 \times 0{\cdot}17}$ =	40·11	3·34	1
H	=	$\frac{0{\cdot}103 \times 2 \times 100}{18 \times 0{\cdot}17}$ =	6·73	6·73	2
O		by difference =	53·16	3·32	1

The empirical formula of the acid is CH_2O (30).

$$\text{The equivalent weight of the acid} = \frac{0{\cdot}13 \times 10000}{21{\cdot}7} = 59{\cdot}90.$$

∴ The molecular formula of the acid is $C_2H_4O_2$ or CH_3COOH.

The acid is, therefore, acetic acid.

(7) 0·358 gm of an aromatic organic acid (A) gave on combustion 0·792 gm. of carbon dioxide, 0·162 gm. of water. 0·179 gm. of the same substance gave 13·03 c.c. of nitrogen at 28°C and 720 m.m. pressure. (A) on boiling with strong hydrochloric acid solution gave another acid (B), 0·183 gm. of which required 15 c. c. of N/10 NaOH for neutralisation. Calcium salt of (B) when distilled with slaked lime gave a hydrocarbon (C). Vapour density of (C) is 39 (H = 1). The filtrate from (B) contains an organic acid (D) which liberates nitrogen when acted by nitrous acid. When neutralised with ammonia and the excess of it was driven out, it gave a characteristic blue colour on addition of a few drops of copper sulphate solution. What are (A), (B), (C) and (D) ?

Find the empirical formula of (A)

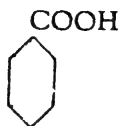
		Per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}792 \times 12 \times 100}{44 \times 0{\cdot}358}$	= 60·34	5·03	9
H	$= \frac{0{\cdot}162 \times 2 \times 100}{44 \times 0{\cdot}358}$	= 5·03	5·03	9
N	$= \frac{273 \times 13{\cdot}03 \times 720 \times 28 \times 100}{301 \times 760 \times 22400 \times 0{\cdot}179}$	= 7·82	0·56	1
O	by difference	= 26·81	1·68	3

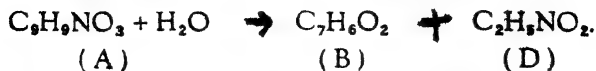
The empirical formula of (A) is $C_9H_9NO_3$.

The substance (C) has a molecular weight (39 × 2 =) 78. As it is derived from an aromatic acid, it must contain a benzene ring. From the molecular weight, the substance is C_6H_6 whose molecular weight is the same as found above.

The equivalent of acid (B)

$$= \frac{0{\cdot}180 \times 10000}{15} = 122.$$

As this acid gives benzene, it must have only one carboxyl group : (122 − 78 = 44, *i. e.*—COO—). The acid (B), therefore, is benzoic acid.

The empirical and eventually the molecular formula of the aromatic acid (A) is $C_9H_9NO_3$ which, from the hydrolysis of HCl, may be supposed to be formed by the condensation of benzoic acid and other soluble acid (D) present in the filtrate from (B). The molecular formula of the acid (D) is

$$\underset{(A)}{C_9H_9NO_3} + H_2O \rightarrow \underset{(B)}{C_7H_6O_2} + \underset{(D)}{C_2H_5NO_2}.$$

The acid (D) liberates nitrogen when acted upon by nitrous acid ; it therefore contains NH_2 group. Subtracting NH_2 and COOH from the molecular formula $C_2H_5NO_2$, we get CH_2 to which obviously the two groups are attached. The acid (D) is,

therefore, glycocoll $NH_2 \cdot CH_2 \cdot COOH$. This is confirmed by the characteristic blue colouration with copper sulphate solution.

The original aromatic acid (A) is then hippuric acid.

The various reactions can be represented as follows :

(8) The bromo derivative of a paraffin when analysed gave the following results :

(*a*) 0·109 gm. of the substance gave 0·088 gm. of carbon dioxide and 0·045 gm. of water.

(*b*) 0·185 gm. of the same substance gave 0·319 gm. silver bromide.

Find the molecular formula of the compound.

		Per cent.	gm. atom	atomic ratio
C	$= \frac{0 \cdot 088 \times 12 \times 100}{44 \times 0 \cdot 109} =$	22·02	1·833	2
H	$= \frac{0 \cdot 045 \times 2 \times 100}{18 \times 0 \cdot 109} =$	4·58	4·58	5
Br	$= \frac{0 \cdot 319 \times 100 \times 80}{188 \times 0 \cdot 185} =$	73·37	0·917	1
		99·97		

The empirical formula is C_2H_5Br which is also the molecular formula.

The substance is Ethyl Bromide.

(9) An aromatic compound (A) gave the following results on analysis :—

0·25 gm. gave 0·638 gm. carbon dioxide and 0·129 gm. water. Further 0·42 gm. gave 38·9 c. c. of dry nitrogen measured at 0°C. and 760 m. m. pressure. (A) gives an oxime containing 20·6°/ₒ nitrogen. (A) condenses with an aliphatic compound (B) containing carbon 54·5°/ₒ, hydrogen 9·1 °/ₒ. The vapour density of (B) is 22. (C) the product of condensation is a heterocyclic compound containing carbon 83·7%, hydrogen 5·5%, nitrogen 10·9°/ₒ. (C) on oxidation yields a dibasic acid (D) containing carbon 50·3°/ₒ, hydrogen 3°/ₒ, nitrogen 8·4°/ₒ. Assign constitutional formula to the compounds (A) to (D) inclusive.

The aromatic compound (A):

		Per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}638 \times 12 \times 100}{44 \times 0{\cdot}25}$	= 69·60	5·80	7
H	$= \frac{0{\cdot}129 \times 2 \times 100}{18 \times 0{\cdot}25}$	= 5·73	5·73	7
N	$= \frac{38{\cdot}9 \times 28 \times 100}{22400 \times 0{\cdot}42}$	= 11·58	0·82	1
O	by difference	= 13·09	0·82	1

The empirical (and probably the molecular) formula of (A) is C_7H_7NO. As it forms an oxime, it must contain an aldehyde group.

The compound (B):

The molecular weight of this compound is (22 × 2 =) 44.

		Per cent.	gm. atom	atomic ratio
C		= 54·5	4·541	2
H		= 9·1	9·100	4
O	by difference	= 36·4	2·275	1

The empirical formula of (B) is C_2H_4O (44).

As the molecular weight is 44, C_2H_4O represents also the molecular formula. The compound is CH_3CHO acetaldehyde. (A) condenses with this; it may, therefore, contain an amino (NH_2) group.

The compound (C):

			Per cent.	gm.atom	atomic ratio
C		=	83·7	6·97	9
H		=	5·50	5·5	7
N		=	10·9	0·78	1
O	is absent.				

The empirical (and probably the molecular) formula is C_9H_7N. On comparing the formulæ of (A), (B) and (C), it will be seen that (C) is formed with the elimination of $2H_2O$. [by condensation of (A) and (B)]

The compound (D):

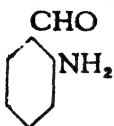
			Per cent.	gm.atom	atomic ratio
C		=	50·3	4·2	7
H		=	3·0	3·0	5
N		=	8·4	0·6	1
O	by difference	=	38·3	2·4	4

The empirical (and probably the molecular) formula of (D) is $C_7H_5NO_4$.

As it is a dibasic acid, it must contain 2 carboxyl groups, and as it is derived from a heterocyclic compound, the remaining atoms C_5H_3N must form the heterocyclic ring which is present in (C). To review the analytical results :—

The compound (A) contains (i) benzene ring (ii) aldehyde group and (iii) an amino group. As the compound (A) condenses with (B) and forms an heterocyclic compound the aldehyde and amino groups are in ortho position with each other. The compound (A) can, therefore, be represented as :

CHO

NH$_2$

o-Amino benzaldehyde (C_7H_7NO).

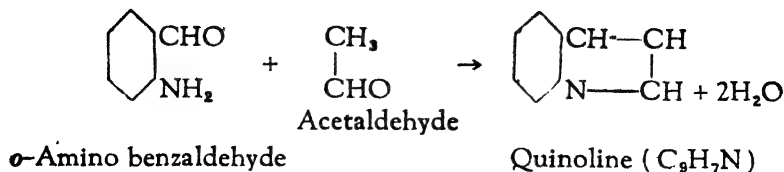
The compound (B) is acetaldehyde CH_3CHO.

It condenses with (A) forming a heterocyclic compound (C) with the elimination of two molecules of water. The reaction can be represented as.

CHO + CH$_3$ → CH—CH

NH$_2$ CHO N—CH + $2H_2O$

Acetaldehyde

o-Amino benzaldehyde Quinoline (C_9H_7N)

The compound (C) gives on oxidation a dibasic acid containing a heterocyclic ring of C_5H_3N. The reaction can be represented thus :

oxidation →

COOH

COOH

N N

Quinoline C_9H_7N

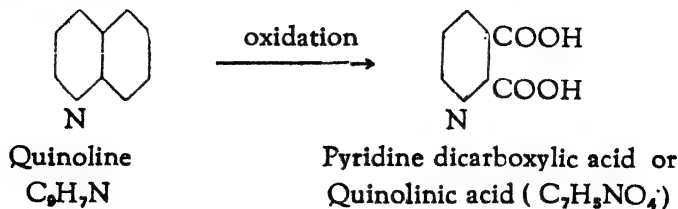
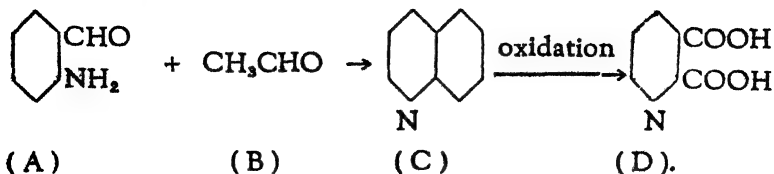
Pyridine dicarboxylic acid or Quinolinic acid ($C_7H_5NO_4$)

To sum up,

CHO + CH_3CHO → oxidation → COOH

NH$_2$ COOH

N N

(A) (B) (C) (D).

(10) The nitro derivative of an aromatic hydrocarbon gave the following results on analysis :—

0·28 gm. gave 0·629 gm. carbon dioxide and 0·129 gm. water. Further 0·18 gm. gave 17·25 c. c. of nitrogen at 27°C. and 710 m. m. pressure. On reduction the above compound gave the product (B) containing 78·5°/₀ carbon ; 8·4°/₀ hydrogen and 13·1°/₀ nitrogen. (B) gave an acetyl derivative (C) which contains 9·4°/₀ nitrogen. (C) on oxidation and hydrolysis gave anthranilic acid. Assign a constitutional formula to the original nitro derivative.

The compound (A) (original nitro derivative of an aromatic compound) :

		Per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}629 \times 12 \times 100}{44 \times 0{\cdot}28}$	= 61·27	5·10	7
H	$= \frac{0{\cdot}129 \times 2 \times 100}{18 \times 0{\cdot}28}$	= 5·12	5·12	7
N	$= \frac{17{\cdot}25 \times 273 \times 710 \times 28 \times 100}{300 \times 760 \times 22400 \times 0{\cdot}18}$	= 10·19	0·73	1
O	by difference	= 23·42	1·46	2

The empirical (and probably the molecular) formula of (A) is $C_7H_7NO_2$ and the compound can be represented as

CH_3 / NO_2 (benzene ring)

o–Nitro toluene.

The CH_3 and NO_2 groups must be in ortho position with respect to each other as the final product is anthranilic acid, *i. e.* *o*–amino benzoic acid.

The substance (B):

		Per cent.	gm. atom	atomic ratio
C	=	78·5	6·54	7
H	=	8·4	8·40	9
N	=	13·1	0·94	1

The empirical (and probably the molecular) formula is C_7H_9N.

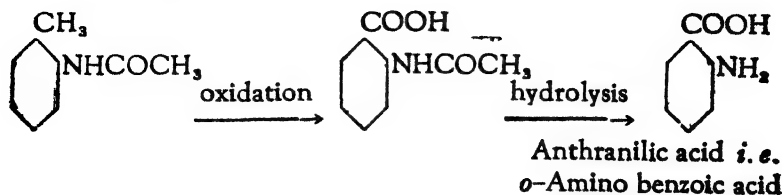
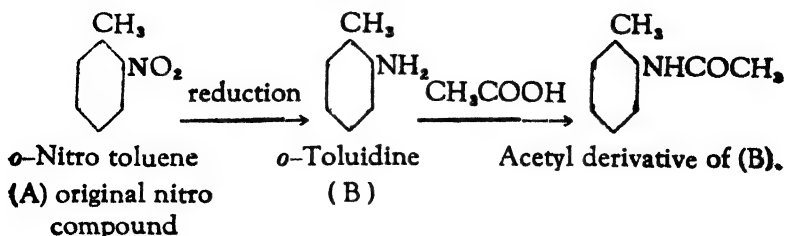
The compound contains an amino (NH_2) group as it is the reduction product of a nitro compound (A). The acetyl derivative will be $C_7H_8NCOCH_3$ which contains $\left(\frac{14 \times 100}{149} = \right)$ 9·396 per cent. nitrogen. This agrees well with the data given 9·4%.

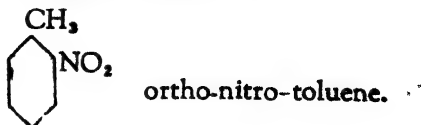
The various reactions can be represented as :

CH_3 / NO_2 (ring) —reduction→ CH_3 / NH_2 (ring) —CH_3COOH→ CH_3 / $NHCOCH_3$ (ring)

o–Nitro toluene (A) original nitro compound; *o*–Toluidine (B); Acetyl derivative of (B).

CH_3 / $NHCOCH_3$ (ring) —oxidation→ $COOH$ / $NHCOCH_3$ (ring) —hydrolysis→ $COOH$ / NH_2 (ring)

Anthranilic acid *i. e.* *o*–Amino benzoic acid

The original compound as assumed before, is

CH_3 / NO_2 (ring) ortho-nitro-toluene.

(11) An aromatic hydrocarbon of vapour density 46 gave the following results on analysis :—0·192 gm. of the substance gave 0·642 gm. carbon dioxide and 0·152 gm. water. On treatment with a mixture of concentrated nitric and sulphuric acids, this hydrocarbon gave two isomeric compounds both containing 61·3% carbon, 5·1% hydrogen and 10·2% nitrogen. What are the structural formulæ of these two isomeric compounds ?

The aromatic hydrocarbon :

			Per cent.	gm. atom	atomic ratio
C	=	$\frac{0.642 \times 12 \times 100}{44 \times 0.192}$ =	91·20	7·60	7
H	=	$\frac{0.152 \times 2 \times 100}{98 \times 0.192}$ =	8·79	8·79	8
			99·99		

The empirical formula is C_7H_8 (92).

The molecular weight of this hydrocarbon is 46 × 2 = 92 Therefore the molecular formula is the same as the empirical one and the hydrocarbon is Toluene $C_6H_5CH_3$. On treatment with nitric and sulphuric acids, ortho and para nitro compounds are formed.

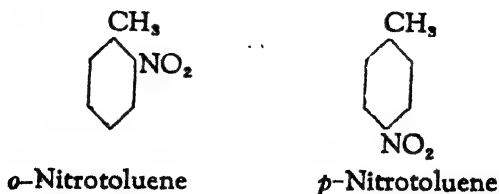
		Per cent.	gm. atom	atomic ratio
C	=	61·3	5·1	7
H	=	5·1	5·1	7
N	=	10·2	0·73	1
O by difference		23·4	1·46	2

The empirical formula of the nitro compound is $C_7H_7NO_2$. The molecular formula is also the same. The two isomeric compounds can be represented as

CH_3 / NO_2 (ring structure)

o–Nitrotoluene

CH_3 / NO_2 (ring structure)

p–Nitrotoluene

(12) A hydrocarbon containing 93·75 per cent. carbon and 6·25 per cent. hydrogen when heated with concentrated sulphuric acid yielded a monosulphonic acid, 0·208 gm. of which required

10 c. c. of $\frac{N}{10}$ caustic soda for neutralisation. On oxidation the hydrocarbon gave a dibasic acid, the anhydride of which when heated with dry ammonia formed an imide. This imide when treated with caustic potash and bromine yielded a monobasic acid containing 10·22 per cent nitrogen. Assign a structural formula to this acid.

The hydrocarbon,

		Per cent.	gm. atom	atomic ratio
C	=	93·75	7·81	5
H	=	6·25	6·25	4

The empirical formula is C_5H_4 (64).

The equivalent weight of the sulphonic acid of the above :

$$= \frac{0{\cdot}208 \times 10000}{10} = 208.$$

The molecular weight of the hydrocarbon can be found by deducting SO_3 (80) from the equivalent weight of the mono sulphonic acid. The molecular weight, therefore is (208 − 80 =) 128. The molecular formula of the hydrocarbon is $C_{10}H_8$. The hydrocarbon is probably naphthalene which on oxidation gives phthalic acid, $C_6H_4(COOH)_2$ – a dibasic acid. This dibasic acid yields an anhydride—phthalic anhydride—which when heated with dry ammonia, gives an imide—phthalimide. When phthalimide is treated with caustic potash and bromine, anthranilic acid $C_6H_4NH_2COOH$ is formed.

The percentage of nitrogen in anthranilic acid is

$\frac{14 \times 100}{137}$ = 10·22, exactly the same as given in the problem.

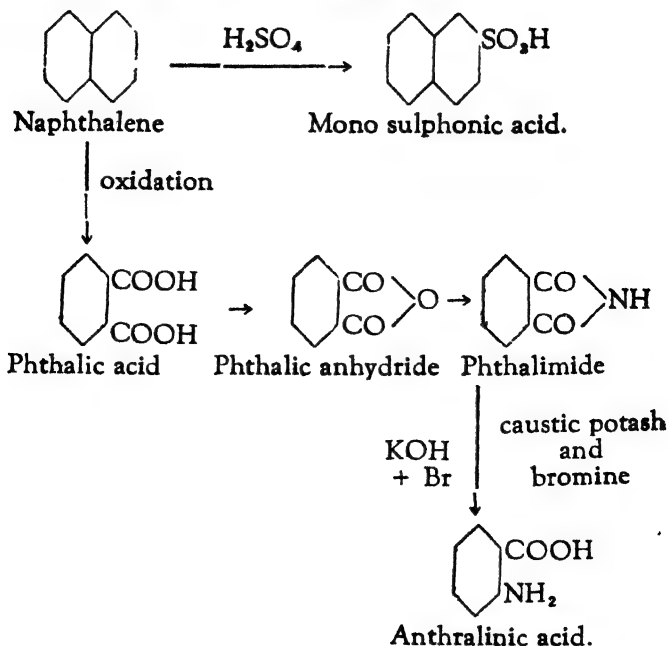
The various reactions are represented as :—

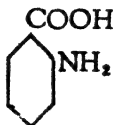
Naphthalene —H_2SO_4→ Mono sulphonic acid (SO_3H).

Naphthalene
| oxidation
↓

Phthalic acid (COOH, COOH) → Phthalic anhydride (CO, CO >O) → Phthalimide (CO, CO >NH)

Phthalimide
| KOH + Br — caustic potash and bromine
↓

Anthralinic acid (COOH, NH_2).

The final product of the series of reactions is anthralinic acid or *o*–amino–benzoic acid

COOH, NH_2

(13) An aromatic monobasic acid (A) gave the following results on analysis :– (*a*) 0·153 gm. gave on combustion 0·289 gm. of carbon dioxide and 0·0462 gm. of water. (*b*) 0·1045 gm. gave 6·58 c. c. of dry nitrogen at 27° C and 710 mm. pressure (*c*) 0·500 gm. required 23·92 c. c. of decinormal sodium hydroxide solution for neutralisation. On treatment with bromine in chloroform solution the acid (A) absorbed bromine and yielded a bromoderivative containing 43·3°/₀ bromine. On reduction

the acid (A) was converted into a second monobasic acid (B) which contained 45·9°/。C, 2·74°/。H, 7·65°/。N and 43·71°/。O. The acid (B) on reduction with tin and hydrochloric acid, diazotisation and boiling with absolute-alcohol, yielded salicylic acid. Heating with zinc dust converted the acid (B) into *p*-nitrobenzoic acid. Assign structural formulæ to (A) and (B).

That, salicylic acid and *p*—nitrobenzoic acid are formed from the acid (B) shows that (OH) and (NO_2) groups are present in that acid and also in the acid (A) and occupy respectively ortho and para positions with respect to COOH in (B) and the side chain containing COOH group in (A).

The monobasic acid (A):

	Per cent.	gm.atom	atomic ratio
$C = \frac{0{\cdot}289 \times 12 \times 100}{44 \times 0{\cdot}153}$	= 52·47	4·37	9
$H = \frac{0{\cdot}0462 \times 2 \times 100}{18 \times 0{\cdot}153}$	= 3·35	3·35	7
$N = \frac{6{\cdot}58 \times 710 \times 273 \times 28 \times 100}{760 \times 22400 \times 300 \times 0{\cdot}1045}$	= 6·69	0·48	1
O by difference	= 37·49	2·34	5

The empirical (and probably the molecular) formula of (A) is $C_9H_7NO_5$ (209).

The equivalent (and molecular) weight of (A):

$$= \frac{0{\cdot}50 \times 10000}{23{\cdot}92} = 209.$$

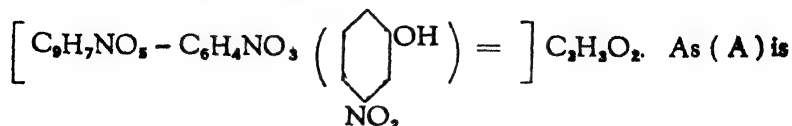
Therefore, the empirical formula is also the molecular formula.

The molecular weight of the bromo derivative of (A).

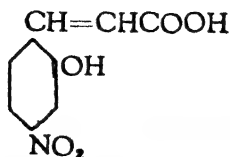
$$= \frac{100 \times 80}{43{\cdot}30} = 184{\cdot}8.$$

The lower value of the molecular weight of the bromo derivative shows that more than one atoms of bromine are added. The

unsaturated linkage takes up bromine in pairs of atoms. At least two atoms of bromine must have been added. The molecular weight of the bromo derivative on this assumption is 369·6. Deducting 2 atoms of bromine (160) will give the molecular weight of the original substance (A). It is (369·6 − 160 =) 209·6— in excellent agreement with the one found above.

This unsaturated linkage (double bond) is in the side chain of (A) which consists of

$$\left[C_9H_7NO_5 - C_6H_4NO_3 \left(\text{(benzene ring with OH and } NO_2) \right) = \right] C_3H_3O_2.$$ As (A) is a monobasic acid, this side chain may be CH=CHCOOH.

The probable structural formula of (A) is

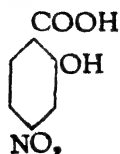
CH=CHCOOH (benzene ring with OH ortho and NO_2 para)

o–Hydroxy *p*–nitro cinnamic acid.

The acid (B):

	Per cent.	gm. atom	atom ratio
C =	45·90	3·825	7
H =	2·74	2·740	5
N =	7·65	0·546	1
O =	43·71	2·732	5

The empirical (and probably the molecular) formula of the acid (B) is $C_7H_5NO_5$ (183).

It has been shown above that the acid (B) contains (OH) and (NO_2) groups in ortho and para positions with respect to COOH group. The structural formula of (B) i

COOH
OH
NO_2

o–Hydroxy *p*–nitro benzoic acid ($C_7H_5NO_5$).
(B)

This acid when heated with zinc dust will lose O of the (OH) group and will give *p*–nitrobenzoic acid. (NO_2) will be replaced by (H) when it is reduced to (NH_2) in acidic reducing solutions, and heated with absolute alcohol after diazotisation.

The various reactions and the structural formulæ of (A) and (B) are given below :—

CH=CH COOH — OH — NO_2 —Bromine→ CHBr—CHBrCOOH — OH — NO_2

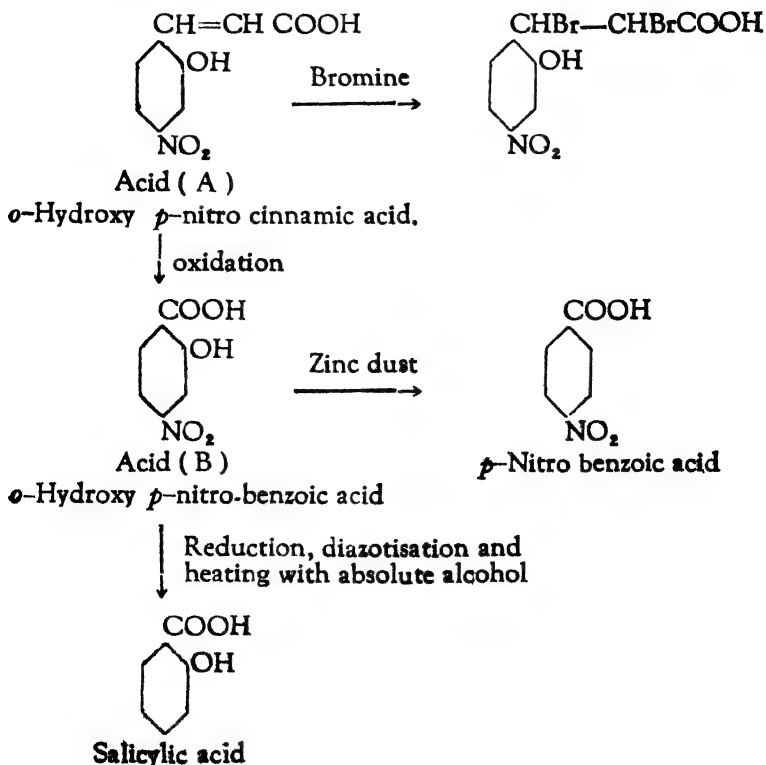
Acid (A)
o–Hydroxy *p*–nitro cinnamic acid.

↓ oxidation

Acid (B) *p*–Nitro benzoic acid
o–Hydroxy *p*–nitro-benzoic acid

↓ Reduction, diazotisation and heating with absolute alcohol

COOH
OH

Salicylic acid

(14) An aromatic monobasic acid (A) containing C, H and O gave the following results on analysis: (*a*) C = 68·85% and H = 4·92%; (*b*) 0·244 gm. of the acid required for neutralisation 20 c.c. of $\frac{N}{10}$ NaOH solution. The acid chloride of (A) on treatment with ammonia gave a compound (B) containing 69·43% C, 5·78%H, 13·22% O and 11·57%N. On distillation with P_2O_5 (B) gave a nitrile (C) which gave the following results on analysis: (*a*) C = 81·55%, H = 4·85%; (*b*) 0·103 gm. gave 11·20 c. c. nitrogen at N. T. P. Assign structural formula to (A), (B) and (C).

The monobasic acid (A):

	Per cent.	gm. atom	atomic ratio
C	= 68·85	5·74	7
H	= 4·92	4·92	6
O by difference	= 26·23	1·64	2

The empirical formula of (A) is $C_7H_6O_2$ (122).

The equivalent and molecular weight of (A)

$$= \frac{0{\cdot}244 \times 10000}{20} = 122.$$

The empirical formula is therefore the molecular formula. The acid can be represented as C_6H_5COOH (Benzoic acid).

The substance (B):

	Per cent.	gm. atom	atomic ratio
C =	69·43	5·785	7
H =	5·78	5·780	7
O =	13·22	0·826	1
N =	11·57	0·826	1

The empirical (and molecular) formula of (B) is C_7H_7NO.

As it is prepared by the action of ammonia on acid-chloride the substance (B) is an amide—benzamide $C_6H_5CONH_2$.

The compound (C) : nitrile,

	Per cent.	gm. atom	atomic ratio
C =	81·55	6·796	7
H =	4·85	4·850	5
N = $\frac{28 \times 11 \cdot 20 \times 100}{22400 \times 0 \cdot 103}$ =	13·59	0·971	1

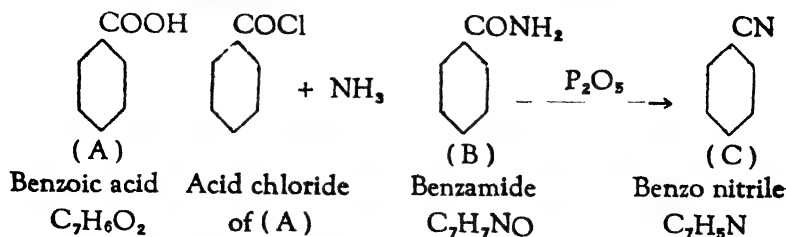
O is absent.

The empirical (and molecular) formula of (C) is C_7H_5N.

As it is a nitrile, it can be represented as C_6H_5 CN.

The various reactions and structural formulæ of (A), (B) and (C) are represented below:—

$$C_6H_5COOH \quad C_6H_5COCl + NH_3 \rightarrow C_6H_5CONH_2 \xrightarrow{P_2O_5} C_6H_5CN$$

COOH	COCl	CONH₂	CN
(A)		(B)	(C)
Benzoic acid	Acid chloride of (A)	Benzamide	Benzo nitrile
$C_7H_6O_2$		C_7H_7NO	C_7H_5N

(**15**) (*a*) An organic substance was found to contain 16·7% chlorine and 0·2125 gm. of it gave 0·484 gm. of carbon dioxide and 0·117 gm. of water. (*b*) 1·062 gm. of the substance when vaporised displaced air that measured 112 c.c. at N·T. P. (*c*) when warmed with a solution of sodium hydroxide, it gave (i) the sodium salt which when heated with soda lime gave chloro-benzene. (ii) The liquid (0·074 gm.) on complete oxidation gave carbon dioxide (0·176 gm.) and water (0·09 gm.). On limited oxidation it gave dimethyl acetaldehyde.

Discuss the constitution of the original substance.

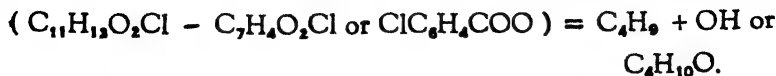
The empirical formula of the original substance :

		Per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}484 \times 12 \times 100}{44 \times 0{\cdot}2125} =$	62·120	5·176	11
H	$= \frac{0{\cdot}117 \times 2 \times 100}{18 \times 0{\cdot}2125} =$	6·119	6 119	13
Cl	given =	16·70	0·470	1
O	by difference =	15 061	0·942	2

The empirical formula is $C_{11}H_{13}O_2Cl$ (212).

$$\text{The molecular weight} = \frac{22400 \times 1{\cdot}062}{112{\cdot}0} = 212{\cdot}4.$$

The empirical formula is therefore the molecular formula. As the substance is hydrolysed by NaOH, it is an ester and as the sodium salt gives chlorobenzene, the ester is one of chlorobenzoic acid. The alcohol forming this ester contains :

($C_{11}H_{13}O_2Cl$ – $C_7H_4O_2Cl$ or ClC_6H_4COO) = C_4H_9 + OH or $C_4H_{10}O$.

The empirical formula of the alcohol (liquid) :

		Per cent.	gm. atom	atom ratio
C	$= \frac{0{\cdot}176 + 12 \times 100}{44 \times 0{\cdot}074} =$	64·71	5·39	4
H	$= \frac{0{\cdot}09 \times 2 \times 100}{18 \times 0{\cdot}074} =$	13·51	13·51	10
O	by difference =	21·78	1·36	1

The empirical formula of the alcohol is $C_4H_{10}O$ and this is also the molecular formula. As the alcohol gives on limited oxidation dimethyl acetaldehyde, it must be dimethyl ethyl alcohol

```
      CH3
      |
   H—C—CH2OH
      |
      CH3
```

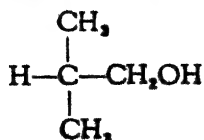
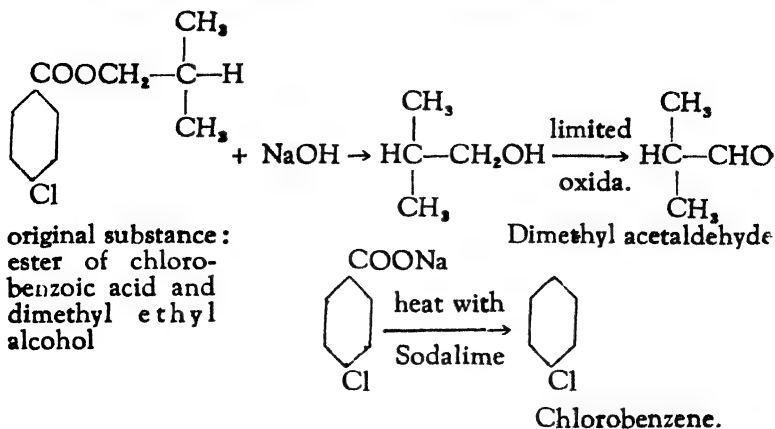
The various reactions can be represented as :—

$$\underset{\text{Cl}}{C_6H_4}\text{—COOCH}_2\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{—H} + NaOH \rightarrow H\underset{CH_3}{\overset{CH_3}{C}}\text{—}CH_2OH \xrightarrow[\text{oxida.}]{\text{limited}} H\underset{CH_3}{\overset{CH_3}{C}}\text{—CHO}$$

original substance: ester of chloro-benzoic acid and dimethyl ethyl alcohol

Dimethyl acetaldehyde

$$\underset{\text{Cl}}{C_6H_4}\text{—COONa} \xrightarrow[\text{Sodalime}]{\text{heat with}} \underset{\text{Cl}}{C_6H_5}$$

Chlorobenzene.

(16) An organic substance (A) gave the following results on analysis : (*a*) 0·123 gm. gave 0·264 gm. carbon dioxide and 0·045 gm. water. (*b*) 0·1845 gm. of the substance gave 16·8 c. c. nitrogen at N. T. P. when heated with iron and hydrochloric acid it gave a substance (B) containing 77·41°/o C, 7·53% H and 15·05% N.

The substance (B) when diazotised and treated with KCN gave a compound (C) which on hydrolysis yielded benzoic acid. Assign structural formulæ to (A), (B) and (C).

The substance (A):

		Per cent.	gm.atom	atomic ratio
C = $\frac{0{\cdot}264 \times 12 \times 100}{44 \times 0{\cdot}123}$	=	58·54	4·88	6
H = $\frac{0{\cdot}045 \times 2 \times 100}{18 \times 0{\cdot}123}$	=	4·06	4·06	5
N = $\frac{16{\cdot}8 \times 28 \times 100}{22400 \times 0{\cdot}1845}$	=	11·38	0·81	1
O by difference	=	26·02	1·62	2

The empirical (and probably the molecular) formula of the substance (A) is $C_6H_5NO_2$.

The substance (B) :

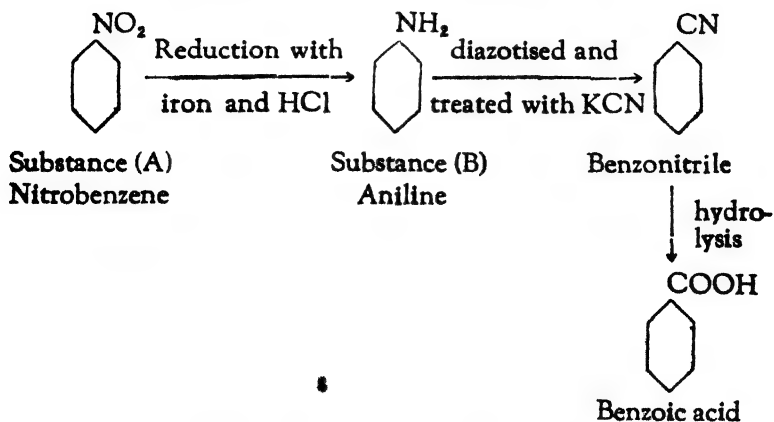
	Per cent.	gm. atom	atomic ratio
C =	77·41	6·45	6
H =	7·53	7·53	7
N =	15·05	1·075	1

O is absent.

The empirical (and probably the molecular) formula of the substance (B) is C_6H_7N.

As the substance (B) is the reduction product of (A) and as it can be diazotised, it must contain NH_2. The formula can be written as $C_6H_5NH_2$.

The substance (C) is formed by diazotising (B) and treating it with KCN in which process the NH_2 group is replaced by CN and benzonitrile C_6H_5CN is formed. Benzonitrile on hydrolysis gives benzoic acid, C_6H_5COOH.

The various reactions and formulæ are given below :

(17) A neutral substance gave the following results on analysis : 0·25 gm. gave 0·6644 gm. CO_2 ; 0·1660 H_2O and 18 c. c. of N at N. T. P. On heating with dilute mineral acid it gave a monobasic acid (A), 0·244 gm. of which required 20 c. c.

$\frac{N}{10}$ NaOH for neutralisation and a base (B) having the vapour density of 22·5. On heating the acid (A) with soda lime benzene was produced. What is the probable structure of the neutral substance ?

The original substance :

		Per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}6644 \times 12 \times 100}{44 \times 0{\cdot}25}$	= 72·48	6·04	9
H	$= \frac{0{\cdot}1660 \times 2 \times 100}{18 \times 0{\cdot}25}$	= 7 37	7·37	11
N	$= \frac{18 \times 28 \times 100}{22400 \times 0{\cdot}25}$	= 9·40	0·67	1
O	by difference	= 10·75	0·67	1

The empirical (and probably the molecular) formula is $C_9H_{11}NO$.

The acid (A):

The equivalent weight $= \frac{0{\cdot}244 \times 10000}{20} = 122.$

The acid gives benzene on heating with soda lime, it must therefore contain a benzene ring and a carboxyl group. It is therefore C_6H_5COOH. This agreees well with the equivalent weight found above.

The base (B) :

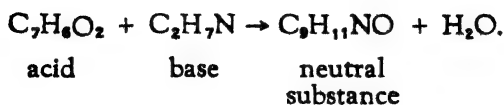
The molecular weight of the base = 22·5 × 2 = 45.

Its empirical formula is $C_9H_{11}NO - C_7H_5O + H = C_2H_7N$.

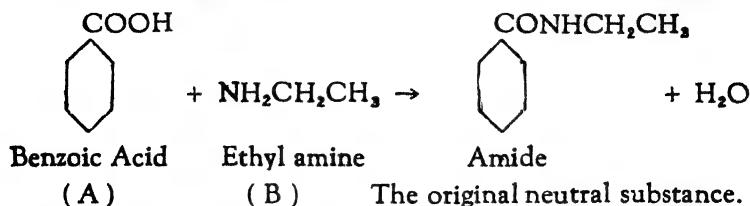
This is in perfect agreement with the molecular weight. As it is a base, it must contain NH_2 group and the structural formula can be written as $C_2H_5NH_2$ or $CH_3CH_2NH_2$ ethyl amine.

The original neutral substance is formed by the action of the acid (A) on the base (B) when one molecule of water is eliminated in the process :

$$C_7H_6O_2 + C_2H_7N \rightarrow C_9H_{11}NO + H_2O.$$

acid base neutral substance

The neutral substance is, therefore, an amide. The reactions and the structural formula of the amide can be represented as :

$$C_6H_5COOH + NH_2CH_2CH_3 \rightarrow C_6H_5CONHCH_2CH_3 + H_2O$$

Benzoic Acid (A) Ethyl amine (B) Amide The original neutral substance.

(18) 0·148 gm. of an aromatic anhydride (A) gave on combustion 0·352 gm. CO_2 and 0·036 gm. H_2O. (A) was condensed with benzene in the presence of aluminium chloride producing a substance (B) having the formula $C_{14}H_8O_2$. On treatment with phenyl hydrazine (B) gave a hydrazone containing 14·43°/$_o$N. The action of bromine on (B) gave a dibromo derivative which on fusion with caustic potash gave alizarine. Assign structural formula to (A) and (B).

The anhydride (A) :

		Per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}352 \times 12 \times 100}{44 \times 0{\cdot}148}$	= 64·87	5·40	8
H	$= \frac{0{\cdot}036 \times 2 \times 100}{18 \times 0{\cdot}148}$	= 2·69	2·69	4
O	by difference	= 32·44	2·03	3

The empirical (and probably the molecular) formula of (A) is $C_8H_4O_3$. As (A) condenses with benzene and gives a compound containing 14 atoms of carbon, its molecule must contain (14 − 6 =) 8 carbon atoms. The empirical formula is therefore the molecular one. Further as it is an anhydride, (A) must contain :

$\begin{matrix} CO \\ CO \end{matrix} \!\!>\!\! O$ group, the remaining group being C_6H_4. The anhydride is

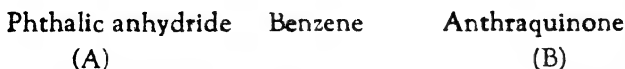
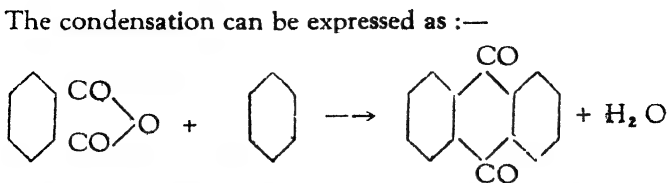
$C_6H_4\begin{matrix} CO \\ CO \end{matrix} \!\!>\!\! O$ Phthalic anhydride.

(A)

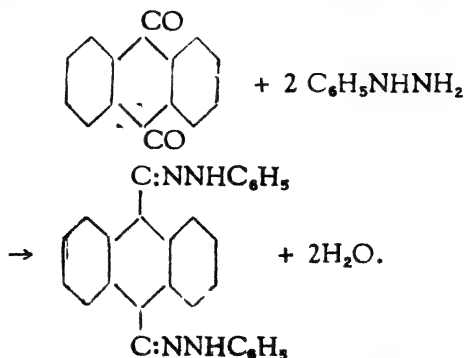
Its condensation with benzene is accompanied by the elimination of water, as is shown by the following equation :—
$C_8H_4O_3 + C_6H_6 \rightarrow C_{14}H_8O_2 + H_2O$.

The condensation can be expressed as :—

$$C_6H_4\begin{matrix} CO \\ CO \end{matrix} \!\!>\!\! O + C_6H_6 \longrightarrow C_6H_4\begin{matrix} CO \\ CO \end{matrix}C_6H_4 + H_2O$$

Phthalic anhydride (A) Benzene Anthraquinone (B)

Anthraquinone gives with phenylhydrazine an hydrazone according to the following equation :—

$$C_6H_4\begin{matrix} CO \\ CO \end{matrix}C_6H_4 + 2\,C_6H_5NHNH_2$$

$$\rightarrow C_6H_4\begin{matrix} C{:}NNHC_6H_5 \\ C{:}NNHC_6H_5 \end{matrix}C_6H_4 + 2H_2O.$$

This hydrazone ($C_{28}H_{20}N_4$) contains $\left(\frac{56 \times 100}{388} = \right)$ 14·43% nitrogen exactly the same as given in the problem.

Anthraquinone gives dibromo derivative which on fusion with caustic potash gives alizarine. The reaction follows the course as shown below :—

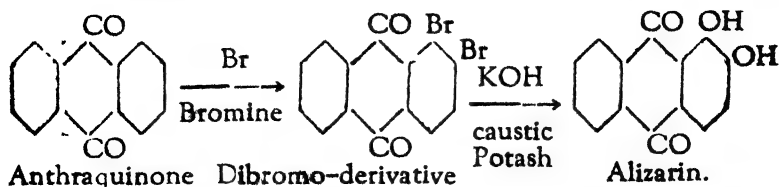
CO CO Br CO OH

Br Br OH

KOH

Bromine caustic

CO CO Potash CO

Anthraquinone Dibromo-derivative Alizarin.

The substances (A) and (B) are:—

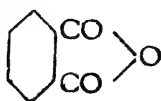
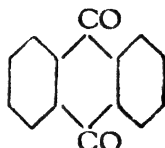
CO

CO

O

CO

CO

(A) (B)

Phthalic anhydride Anthraquinone.

(19) An ester of a monobasic acid gave on analysis the following results:—

C = 75·88°/₀; H = 5·75°/₀; O = 18·4°/₀. It is dissolved in conc. H_2SO_4 and the solution poured in water. The resulting substance (A) gave on analysis :—C = 68·75°/₀; H = 6·25°/₀; O = 25°/₀. The substance (A) readily reacts with metallic sodium in alcoholic solution and the sodium compound on treatment with CH_3I gave a substance (B) which on analysis gave :—C = 69·9°/₀; H = 6·8°/₀; O = 23·3°/₀. The substance (A) when treated with dilute alkali in the cold gave a crystalline acid (C) which gave on analysis :— C = 65·85°/₀; H = 4·87°/₀; O = 29·27°/₀. When the substance (C) is heated with dilute H_2SO_4, CO_2 is evolved and acetophenone is formed. Assign possible formula for the original ester and for the compounds (A), (B) and (C).

The empirical formula of the ester :—

	per cent.	gm. atom	atomic ratio	
C	75·88	6·32	5·5	11
H	5·75	5·75	5·0	10
O	18·4	1·15	1	2

The empirical formula is :—$C_{11}H_{10}O_2$.

The substance (A) on analysis contains the elements :—

	per cent.	gm. atom	atomic ratio	
C	68·75	5·73	3·67	11
H	6·25	6·25	4	12
O	25·0	1·56	1	3

The empirical formula of (A) is $C_{11}H_{12}O_3$.

The compound (A) $C_{11}H_{12}O_3 \xrightarrow[CH_3I]{Na}$ (B) containing

	per cent.	gm. atom	atomic ratio	
C	69·9	5·825	4	12
H	6·8	6·8	4·7	14
O	23·30	1·456	1	3

The empirical formula of (B) is $C_{12}H_{14}O_3$.

The compound (A) $C_{11}H_{12}O_3 \xrightarrow[alkali]{dil.}$ (C) containing

	per cent.	gm. atom	atomic ratio	
C	65·85	5·49	3	9
H	4·87	4·87	2·67	8
O	29·27	1·83	1	3

The empirical formula of (C) is $C_9H_8O_3$.

The compound (C) $C_9H_8O_3 \xrightarrow[dil\ H_2SO_4]{heated}$ acetophenone and CO_2.

The empirical formula of acetophenone is C_8H_8O having the constitutional formula $C_6H_5COCH_3$.

The summary of the results of analysis and of the reactions gives indication of the structure of A, B, and C.

The acid (C) $C_9H_8O_3$ gives acetophenone $C_6H_5COCH_3$ and carbon dioxide. It can therefore be represented as

$$C_6H_5COCH_2COOH.$$

This acid is formed by hydrolysis of the ester (A) $C_{11}H_{12}O_3$ which has C_2H_4 more than the acid. The ester (A) is therefore

$$C_6H_5COCH_2COOC_2H_5.$$

This ester (A) is formed from the original ester with the help of H_2SO_4. The original ester $C_{11}H_{10}O_2$ can therefore be represented as

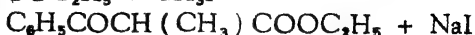
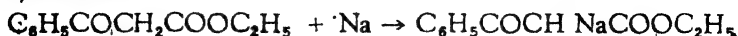
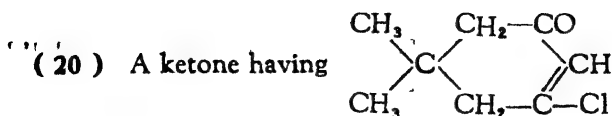
$$C_6H_5C \vdots C{\cdot}COOC_2H_5.$$

The CH_2 group in the ester (A) $C_6H_5COCH_2COOC_2H_5$ is between two carbonyl groups; its hydrogen atoms therefore have an acidic reaction; and can be replaced by Na. The Na compound reacts with CH_3I and gives (B). The reactions can be represented as

$$C_6H_5COCH_2COOC_2H_5 + Na \rightarrow C_6H_5COCH\,NaCOOC_2H_5$$

$$C_6H_5COCH\,NaCOOC_2H_5 + CH_3I \rightarrow$$
$$C_6H_5COCH\,(CH_3)\,COOC_2H_5 + NaI$$
$$\text{(B)}$$

(20) A ketone having

```
CH3      CH2—CO
   \    /      \
    >C<         >CH
   /    \      //
CH3      CH2—C—Cl
```

as structural formula, was reduced with sodium alcoholate. The resultant product gave the following results on analysis :—

(*a*) 0·1499 g. of the compound yielded on combustion 0·3835 g. of CO_2 and 0·1559 g. of H_2O.

(*b*) 0·3445 g. of the same, when reduced with hydriodic acid, yielded ethyl iodide corresponding to 0·4704 gm. of AgI.

(*c*) The product when treated with acetyl chloride was converted into another product which contained 67·33 % C, 10·41 % H. What are the most probable structural formulæ of the compounds.

(*a*) The empirical formula from the results of analysis is :—

		per cent.	gm. atom	atomic ratio
C	$= \frac{0·3835 \times 12 \times 100}{44 \times 0·1499}$	= 69·78	5·81	5
H	$= \frac{0·1559 \times 2 \times 100}{18 \times 0·1499}$	= 11·54	11·54	10
O	= by difference	= 18·68	1·16	1

The empirical formula of the compound (*a*) is $C_5H_{10}O$. The molecular formula of the orignal ketone is $C_8H_{11}OCl$.

∴ The molecular formula of the compound (*a*) must have more than 8 carbon atoms. In the reaction.

$$\begin{matrix} CH_3 & & CH_2—CO & \\ & \rangle C \langle & & \rangle CH \\ CH_3 & & CH_2—C—Cl & \end{matrix} + C_2H_5ONa$$

reduction, and substitution of Cl by OC_2H_5 group take place and

$$\begin{matrix} & & H \quad OH & \\ CH_3 & & CH_2—C & \\ & \rangle C \langle & & \rangle CH_2 \\ CH_3 & & CH_2—CH & \\ & & OC_2H_5 & \end{matrix} + NaCl \text{ are formed.}$$

$(C_{10}H_{20}O_2)$ (a)

The molecular wt. of (*a*) is 172.

The molecular wt. of (*a*) as obtained from results in (*b*) is $\frac{0·3445 \times 235}{0·4704} = 172.$

The empirical formula of the compound (c)

	per cent.	gm. atom	atomic ratio
C	67·33	5·61	12
H	10·41	10·41	22
O by difference	22·26	1·39	3

The compound is $C_{12}H_{22}O_3$.

Compound (c) is obtained by reacting the compound (*a*) with acetyl chloride :

$$C_{10}H_{20}O_2 + CH_3COCl = C_{12}H_{22}O_3 + HCl$$

The structure, therefore, is

CH₃ and CH₃ on C; ring: C—CH₂—CH(—CH₂—COOCCH₃)—CH₂—CH(OC₂H₅)—CH₂—C

$$(CH_3)_2C\langle\begin{matrix} CH_2-\overset{H}{C}H(CH_2COOCCH_3) \\ CH_2-CH(OC_2H_5) \end{matrix}\rangle CH_2$$

The various reactions can be represented as :

Original substance $C_8H_{11}OCl$:

$$(CH_3)_2C\langle\begin{matrix} CH_2-CO \\ CH_2-C-Cl \end{matrix}\rangle CH$$

Reduction + C_2H_5ONa ↓

Product (a) $C_{10}H_{20}O_2$

$$(CH_3)_2C\langle\begin{matrix} CH_2-\overset{H}{C}(OH) \\ CH_2-\overset{H}{C}(OC_2H_5) \end{matrix}\rangle CH_2$$

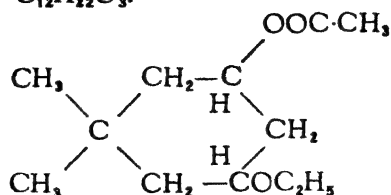
Original substance + C_2H_5O + 4H − Cl. This contains OH group as it is acted by acetyl chloride.

Mol. wt. is confirmed by (b)

Product (a) $C_{10}H_{20}O_2$ with CH_3COCl

↓ ($C_{10}H_{19}O_2$ + $OC{\cdot}CH_3$) H of OH being eliminated as HCl.

Product (c) $C_{12}H_{22}O_3$.

```
                              OOC·CH3
                             /
 CH3        CH2—C
    \      /    H \
      C              CH2
    /      \    H  /
 CH3        CH2 —COC2H5
```

(21) A monobasic acid (A) gave the following results on analysis :— 0·1430 gm. gave 0·3465 gm. CO_2 and 0·0592 gm. H_2O. 0·2546 gm. required 11·7 c. c. of N/10 NaOH for exact neutralisation. On treatment with bromine (A) gave a compound (B) which was analysed with the following results : 0·1821 gm. gave 0·1787 gm. CO_2 and 0·0304 gm. H_2O ; 0·1520 gm. gave 0·2124 gm. AgBr. 0·1944 gm. of (B) when dissolved in 10 gms. benzene lowered the freezing point by 0·18°C. (When a gram mol. is dissolved in 100 gm. benzene the depression of the freezing point is 50°C). Oxidation of (A) gave first a compound of the formula $C_8H_6O_3$ and subsequently an acid $C_8H_6O_4$ which on heating with hydrochloric acid yielded protocatechuic acid viz. 3 : 4—dihydroxy benzoic acid. Assign a structure to the acid (A) giving reasons.

Empirical formula of acid (A) is

	per cent.	gm. atom	atomic ratio	
$C = \frac{12 \times 0{\cdot}3465 \times 100}{44 \times 0{\cdot}1430}$	= 66·09	5·51	3	6
$H = \frac{0{\cdot}0592 \times 2 \times 100}{18 \times 0{\cdot}1430}$	= 4·60	4·60	2·5	5
O by difference	= 29·31	1·83	1	2

∴ The Empirical formula of (A) is $C_6H_5O_2$. (109)

Further the equivalent weight of (A) is $= \dfrac{0{\cdot}2546 \times 10000}{11{\cdot}7}$

$= 217{\cdot}6$ or 218

∴ The mol. formula of the monobasic acid (A) is $C_{12}H_{10}O_4$

The empirical formula of the bromo-derivative (B) is obtained thus :

		per cent.	gm.atom	atomic	ratio
C	$= \dfrac{0{\cdot}1787 \times 12 \times 100}{44 \times 0{\cdot}1821}$	= 26·76	2·23	3	6
H	$= \dfrac{0{\cdot}034 \times 2 \times 100}{18 \times 0{\cdot}1821}$	= 1·85	1·85	2·5	5
Br	$= \dfrac{0{\cdot}2124 \times 80 \times 100}{188 \times 0{\cdot}1520}$	= 59·46	0·74	1	2
O	by difference	11·93	0·74	1	2

The empirical formula of (B) is $C_6H_5O_2Br_2$. (269). The molecular weight must be double this as the original acid contains $C_{12}H_{10}O_4$. This is confirmed by the lowering of the freezing point of benzene as given below :—

$$\frac{100 \times 0{\cdot}1944 \times 50}{0{\cdot}18 \times 10} = 540.$$

The molecular formula of (B) is, therefore, $C_{12}H_{10}O_4Br_4$. So the monobasic acid (A) gives a tetrabromo derivative (B) as an addition product.

∴ The substance (A) is an unsaturated acid with two double bonds.

Further the substance (A) on oxidation gives $C_8H_6O_3$

∴ (A) contains a side chain.

As $C_8H_6O_3$ gives on further oxidation an acid $C_8H_6O_4$

∴ $C_8H_6O_3$ is an aldehyde.

The acid $C_8H_6O_4$ on heating with HCl gives protocatechuic acid.

COOH (benzene ring) OH, OH

The structural formulæ of the monobasic acid (A) and the various compounds resulting from it are :—

CH = CH·CH = CH·COOH (on benzene ring with O—CH₂—O group) —Bromination→ CHBr·CHBr·CHBr·CHBr·COOH (on benzene ring with O—CH₂—O group)

Monobasic acid (A) $C_{12}H_{10}O_4$ Piperic acid

Tetra bromo piperic acid

↓ Oxidation

CHO (on benzene ring with O—CH₂—O group)

Piperonal $C_8H_6O_3$

↓ Further oxidation

COOH (on benzene ring with O—CH₂—O group)

Piperonylic acid $C_8H_6O_4$

↓ Heating with HCl

COOH (benzene ring) OH, OH

Protocatechuic acid $C_7H_6O_4$

(22) An organic acid capable of yielding a trialkyl derivative, has the molecular weight of 168 and analyses as follows : (*a*) 0·1 gm. of the substance gave 0·02143 gm. of H_2O ; and 0·13095 gm. CO_2 ; and 26·66 c. c. of nitrogen at N. T. P.

The sodium salt of that acid, on treatment with $POCl_3$, yielded a hydroxy dichloro derivative, which analyses as follows : (*b*) 0·1 gm. of the substance gave 0·14 gm. AgCl, 0·1073 gm. CO_2; 0·00878 gm. H_2O ; and 21·85 c. c. nitrogen at N. T. P.

The above hydroxy dichloro derivative can be changed into a trichloro one by means of PCl_5. The resulting substance which loses all its oxygen, analyses as follows : (*c*) 0·1 gm. of the substance gave 0·1920 gm. of AgCl; 0·09843 gm. CO_2, and 0·00403 gm. H_2O and 20 c. c. of nitrogen at N. T. P.

The trichloro derivative on treatment with HI at 0°C and then on further treatment with H_2O and Zn dust, gave a substance having the formula $C_5H_4N_4$. The original acid on oxidation with cold HNO_3 left in tact a six membered ring compound and carbamide was split off. With $KMnO_4$ solution it left behind a five membered ring compound.

What is the probable nature and constitution of the original acid and various derivatives above mentioned ?

The empirical formula of the organic acid is :—

		per cent.	gm.atom	atomic ratio
C =	$\frac{0{\cdot}13095 \times 12 \times 100}{44 \times 0{\cdot}1}$	35·73	2·98	5
H =	$\frac{0{\cdot}02143 \times 2 \times 100}{18 \times 0{\cdot}1}$	2·38	2·38	4
N =	$\frac{26{\cdot}66 \times 28 \times 100}{22400 \times 0{\cdot}1}$	33·34	2·38	4
O	by difference	28·55	1·78	3

∴ The empirical formula of the original acid is $C_5H_4N_4O_3$. This is as well its molecular formula.

(*b*) The hydroxy dichloro derivative :

		per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}1073 \times 12 \times 100}{44 \times 0{\cdot}1} =$	29·25	2·44	5
H	$= \frac{0{\cdot}00878 \times 2 \times 100}{18 \times 0{\cdot}1} =$	0·976	0·976	2
N	$= \frac{21{\cdot}85 \times 28 \times 100}{22400 \times 0{\cdot}1} =$	27·32	1·94	4
Cl	$= \frac{0{\cdot}14 \times 35{\cdot}5 \times 100}{143{\cdot}5 \times 0{\cdot}1} =$	34·63	0·98	2
O	by difference	7·824	0·49	1

∴ The empirical formula of (*b*) is $C_5H_2Cl_2N_4O$.

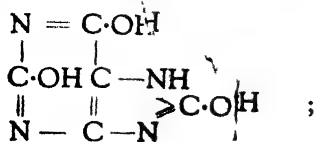
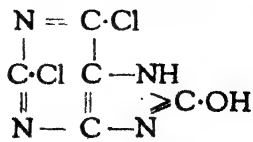
(*c*) The trichloro derivate :

		per cent.	gm.atom	atomic ratio
C	$= \frac{0{\cdot}09843 \times 12 \times 100}{44 \times 0{\cdot}1} =$	26·84	2·24	5
H	$= \frac{0{\cdot}00403 \times 2 \times 100}{18 \times 0{\cdot}1} =$	0·448	0·448	1
N	$= \frac{20 \times 28 \times 100}{22400 \times 0{\cdot}1} =$	25·00	1·79	4
Cl	$= \frac{0{\cdot}1920 \times 35{\cdot}5 \times 100}{143{\cdot}5 \times 0{\cdot}1} =$	47·50	1·339	3

O is absent as the total of percentages is 99·788 or nearly 100.

The empirical formula of (*c*) is $C_5HCl_3N_4$.

The structural formula of the original organic acid and the various derivatives are as follows :—

```
N = C·OH                          N = C·Cl
|    |                            |    |
C·OH C —NH                        C·Cl C —NH
||   ||    >C·OH        ;         ||   ||    >C·OH
N —  C —N                         N —  C —N
```

Organic acid
$C_5H_4N_4O_3$
Uric acid.
(*a*)

Hydroxy dichloro comp.
$C_5H_2Cl_2N_4O$
2 : 6-dichloro 8-hydroxy purine.
(*b*)

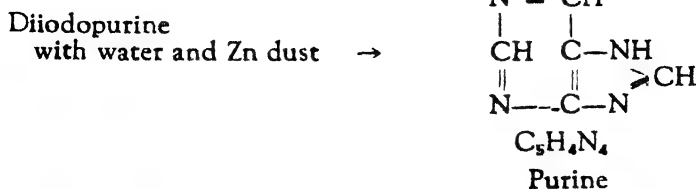
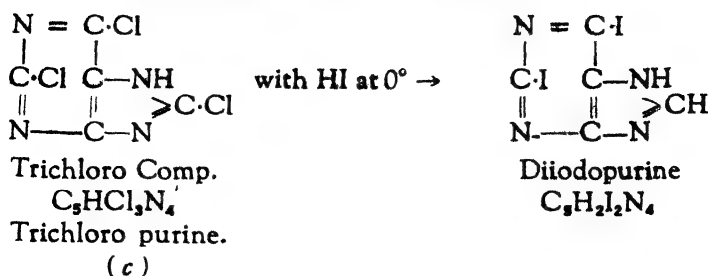
```
N = C·Cl                                   N = C·I
|    |                                     |    |
C·Cl C—NH         with HI at 0° →          C·I  C—NH
||   ||   >C·Cl                            ||   ||   >CH
N———C—N                                    N.——C—N
Trichloro Comp.                            Diiodopurine
   C5HCl3N4                                  C5H2I2N4
Trichloro purine.
```

Trichloro Comp. $C_5HCl_3N_4$ Trichloro purine. → Diiodopurine $C_5H_2I_2N_4$

(*c*)

```
                                           N = CH
Diiodopurine                               |    |
  with water and Zn dust      →            CH   C—NH
                                           ||   ||   >CH
                                           N——.C—N
```

$C_5H_4N_4$

Purine

Further, reactions of the original acid (a) confirm its structure :—

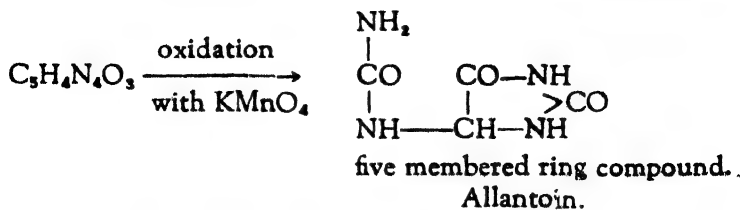
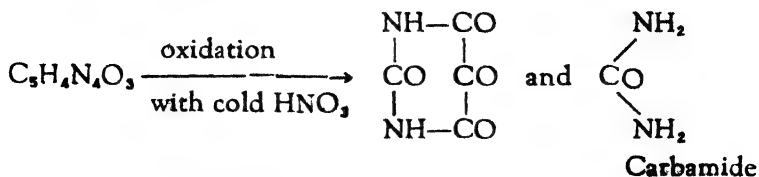
```
                                 NH—CO               NH2
              oxidation          |    |             /
C5H4N4O3 ——————————————→         CO   CO   and    CO
          with cold HNO3         |    |             \
                                 NH—CO               NH2
                                                  Carbamide
```

$C_5H_4N_4O_3 \xrightarrow[\text{with cold } HNO_3]{\text{oxidation}}$ Alloxan + Carbamide

```
                                 NH2
              oxidation          |
C5H4N4O3 ———————————→            CO      CO—NH
          with KMnO4             |       |     >CO
                                 NH——————CH—NH
```

$C_5H_4N_4O_3 \xrightarrow[\text{with } KMnO_4]{\text{oxidation}}$

five membered ring compound.

Allantoin.

(23) A ketone of a dicyclic terpene 0·152 gm. in weight, when dissolved in 50 gm. of C_6H_6 showed 0·1°C as the depression of the F. P. On oxidation, the ketone gave a dibasic acid, the anhydride of which gave the following results on analysis :— 0·091 gm. of the substance gave 0·22 gm. CO_2 and 0·063 gm. H_2O. This anhydride on reduction with sodium amalgam produced a substance (A) which on analysis gave C = 71·43%; H = 9·52%.

On treatment with KCN the substance (A) gave a nitrile of a K salt of the formula $C_{11}H_{16}O_2NK$.

This nitrile when hydrolysed produced a dibasic acid (B) which on combustion gave C = 61·69°/₀; and H = 8·41°/₀. The calcium salt of (B) gave the original ketone on distillation.

What conclusions would you draw with regard to the probable constitution of the various substances ? (When a gram molecule is dissolved in 100 gm. C_6H_6 depression of the F. P. = 50°C).

The molecular weight of the ketone of the dicyclic terpene is :—

$$\text{Mol. Wt.} = \frac{K \times 100 \times a}{\Delta\, b} = \frac{50 \times 100 \times 0{\cdot}152}{0{\cdot}1 \times 50} = 152.$$

The anhydride of the dibasic acid :

			per cent.	gm. atom	atomic ratio
C	$= \frac{0{\cdot}22 \times 12 \times 100}{44 \times 0{\cdot}091}$	=	65·94	5·5	10
H	$= \frac{0{\cdot}063 \times 2 \times 100}{18 \times 0{\cdot}091}$	=	7·69	7·69	14
O	by difference	=	26·37	1·65	3

The empirical formula of the anhydride is $C_{10}H_{14}O_3$.

The substance (A) obtained on reduction of the anhydride $C_{10}H_{14}O_3$.

	per cent	gm. atom	atomic ratio
C	71·43	5·95	10
H	9·52	9·52	16
O by difference	19·05	1·19	2

∴ The empirical as well as the molecular formula of (A) is $C_{10}H_{16}O_2$ because

$$C_{10}H_{16}O_2 + KCN \rightarrow C_{11}H_{16}O_2NK$$

(A) Nitrile of a K salt

The nitrile on hydrolysis produces a dibasic acid (B)

The dibasic acid (B)

		per cent.	gm. atom	atomic ratio
C		61·69	5·14	11
H		8·41	8·41	18
O	by difference	29·9	1·87	4

The empirical formula of the dibasic acid (B) is $C_{11}H_{18}O_4$

The ketone is of dicyclic terpene class and its molecular wt. is 152.

∴ It is camphor : $C_{10}H_{16}O$.

```
CH2———CH——— CH2
|            |            |
| CH3 — C —CH3 |    oxidation           CH2———CH———COOH
|            |            |   ——————→          |            |
CH2———C————CO                            | CH3 — C—CH3
             |                                   |            |
            CH3                                CH2———C————COOH
                                                              |
                                                             CH3
```

Camphor : $C_{10}H_{16}O$. Camphoric acid

```
   CH2———CH ———CO                          CH2———CH———CH2
→ |  CH3 —C —CH3 >O     sodium      |  CH3 —C—CH2 >O
   CH2———C————CO      ————→        CH2———C————CO
              |                 amalgam                  |
             CH3                                        CH3
```

Camphoric anhydride $C_{10}H_{14}O_3$

Campholide $C_{10}H_{16}O_2$ (A)

```
           CH2———CH———CH2CN
   KCN  |  CH3 —C —CH3 hydrolysis   CH2——CH——CH2COOH
A ————→ |            |      ——————→    |  CH3-C—CH3
           CH2———C———COOK               CH2——C——COOH
                      |                                  |
                     CH3                               CH3
```

Nitrile of K salt $C_{11}H_{16}O_2NK$

Homo camphoric acid, $C_{11}H_{18}O_4$, (dibasic acid) (B)

```
CH2———CH———CH2—COO                                CH2———CH———CH2
|      |            \                             |      |      |
| CH3 - C - CH3      Ca                           | CH3 - C - CH3 |
|      |            /       Distillation          |      |      |
CH2———C———COO               ———————→              CH2———C———CO
       |                                                 |
      CH3                                               CH3
```

Ca–salt of the dibasic acid (B) — Camphor $C_{10}H_{16}O$.

(24) A neutral organic substance gave on combustion the following data :— 56·8% C ; 9·5% H and 33·7% O; 1·266 gm. when converted into vapour gave a volume calculated at N. T. P., of 149·33 c. c. When warmed with a solution of KOH it was decomposed giving (*a*) the K salt of an acid and (*b*) a liquid.

(*a*) The free acid on combustion gave 48·7% C; 8·1% H and 43·2% O and its silver salt contained 42·35% Ag. In a Zeisel determination 0·296 gm. of the acid gave 0·940 gm. of AgI. (*b*) The liquid on analysis gave 60% C ; 13·3% H ; 26·7% O, and on oxidation gave another neutral body containing 62·1% C ; 10·3% H ; and 27·6% O ; and its vapour density was 29. What conculsions do you draw as to the nature and constitution of the material ? (Ag = 108 ; I = 127).

The empirical formula of the neutral substance which is obviously an ester is :

	per cent.	gm. atom	atomic ratio
C	56·8	4·73	9
H	9·5	9·5	18
O	37·7	2·1	4

∴ The empirical formula is $C_9H_{18}O_4$.

Further its mol. wt. is

$$\frac{1{\cdot}266 \times 22400}{149{\cdot}33} = 19^{0}$$

∴ its mol. formula is $C_9H_{18}O_4$

(*a*) The free acid.

	per cent	gm. atom	atomic ratio
C	48·7	4·06	3
H	8·1	8·1	6
O	43·2	2·7	2

∴ The empirical formula is $C_3H_6O_2$

The equivalent wt. and eventually the mol. wt. of (*a*) can be obtained from the percentage of Ag in its silver salt:

$$\frac{100 \times 108}{42{\cdot}35} - 108 + 1 = 255 - 107 = 148$$

∴ The mol. formula of (*a*) is $C_6H_{12}O_4 = C_5H_{11}O_2COOH$.

The number of ethoxy or methoxy groups (Zeisel method)

$$\frac{148 \times 0{\cdot}94}{0{\cdot}296 \times 235} = 2$$

The three possible acids are :—

2 methoxy groups : $(CH_3O)_2\ C_3H_5COOH$

2 ethoxy groups : $(C_2H_5O)_2\ CHCOOH$

1 methoxy and 1 ethoxy group :

$(CH_3O)(C_2H_5O)\ C_2H_3COOH$.

(*b*) The liquid must be a alcohol and a secondary one as it gives on oxidation a neutral substance—a ketone.

	per cent	gm. atom	atomic ratio
C	60	5	3
H	13·3	13·3	8
O	26·7	1·7	1

∴ The empirical formula is C_3H_8O, and the probable structure ($CH_3CHOHCH_3$). The oxidation product of the liquid (b):

	per cent	gm. atom	atomic ratio
C	62·1	5·2	3
H	10·3	10·3	6
O	27·6	1·7	1

∴ The empirical formula is C_3H_6O.

Its vapour density is 29 ∴ the mol. formula is C_3H_6O (58). Acetone.

The original neutral substance is therefore an ester of iso-propyl alcohol of one of the acids given above.

(25) 0·142 gm. of a heterocyclic organic compound (A) gave on combustion 0·176 gm. CO_2 and 0·018 gm. water. Also 0·200 gm. gave 37·2 c. c. nitrogen at 27·C, and 710 m. m..(A) gives an oxime (B) having 30·6% C, 26·8% N, and 1·9% H. On reduction this oxime yields a compound (C) having 33·6°/₀C, 29·4°/₀ N and 3·5°/₀ H. Cyanic acid reacts with (C) and gives uric acid. Suggest constitutional formulæ for (A), (B) and (C). Are there any other possible formulæ for the same compounds ?

The heterocyclic Compund (A).

	Per cent.	gm.atom	atomic ratio
$C = \frac{0 \cdot 176 \times 12 \times 100}{44 \times 0 \cdot 142} =$	33·8	2·8	2
$H = \frac{0 \cdot 018 \times 2 \times 100}{18 \times 0 \cdot 142} =$	1·41	1·41	1
$N = \frac{37 \cdot 2 \times 710 \times 273 \times 28 \times 100}{300 \times 760 \times 0 \cdot 200 \times 22400} =$	19·77	1·41	1
O by difference	45·02	2·81	2

∴ The empirical formula of comp. (A) is C_2HNO_2.

The oxime (B).

	Per cent	gm. atom	atomic ratio
C	30·6	2·55	4
H	1·9	1·9	3
N	26·8	1·91	3
O by difference	40·7	2·54	4

∴ The empirical formula of oxime (B) is $C_4H_3N_3O_4$.

∴ The molecular formula of (A) is $C_4H_2N_2O_4$.

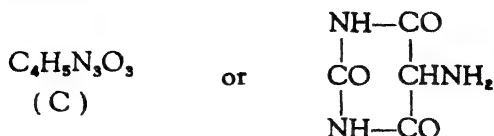
The compound (C)

		Per cent.	gm. atom	atomic ratio
C		33·6	2·8	4
H		3·5	3·5	5
N		29·4	2·1	3
O	by difference	33·5	2·1	3

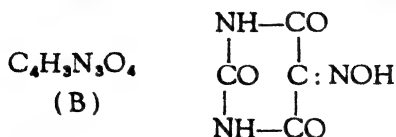
∴ The empirical formula of compound (C) is $C_4H_5N_3O_3$. Cyanic acid reacts with (C) and gives uric acid.

∴ Compound (C) is uramil.

$C_4H_5N_3O_3$ (C) or

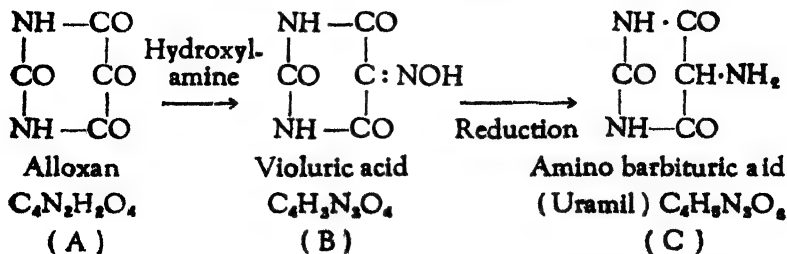
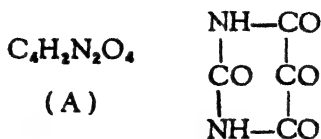
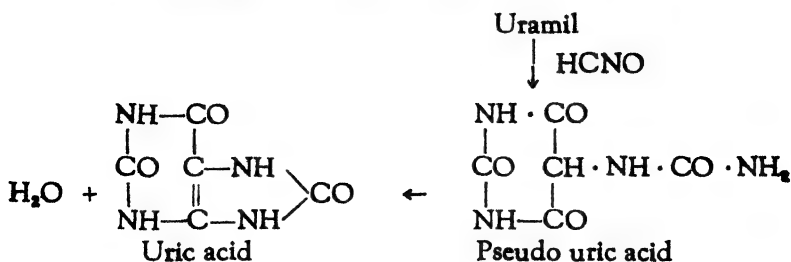
```
NH—CO
|    |
CO   CHNH2
|    |
NH—CO
```

As the uramil (C) is obtained by the reduction of the oxime (B) the compound (B) is violuric acid

$C_4H_3N_3O_4$ (B)

```
NH—CO
|    |
CO   C : NOH
|    |
NH—CO
```

As the oxime (B) is obtained from (A), the latter compound is alloxan.

$C_4H_2N_2O_4$ (A)

```
NH—CO
|    |
CO   CO
|    |
NH—CO
```

```
                                      Uramil
                                        | HCNO
                                        ↓
        NH—CO                         NH · CO
        |   |                         |    |
        CO  C—NH                      CO   CH · NH · CO · NH2
H2O +   |   ||    >CO        ←        |    |
        NH—C—NH                       NH—CO
        Uric acid                     Pseudo uric acid
```

(26) An acid derived from p-xylene ($CH_3C_6H_4CH_3$) gave the following results on analysis :—3·240 mg. gave 8·03 mg. CO_2 and 2·86 mg. H_2O. When treated with bromine it was converted into a bromoderivative containing 36·2°/ₒ of bromine, and this when digested with alcoholic potash, yielded an acid which gave the following results on analysis : 3·400 mg. gave 8·552 mg. CO_2 and 2·618 mg. H_2O. What can you deduce from the results ?

The acid from p-xylene.

		Per cent.	gm. atom	atomic ratio
C	$= \frac{8·03 \times 12 \times 100}{44 \times 3·24} =$	67·6	5·63	4
H	$= \frac{2·86 \times 2 \times 100}{18 \times 3·24} =$	9·8	9·80	7
O	by difference	22·6	1·41	1

The empirical formula of the acid is C_4H_7O.

The acid is derived from p-xylene and it must contain 2 oxygen atoms. The molecular formula of the acid is therefore $C_8H_{14}O_2$. The bromoderivative of the acid will be $C_8H_{13}BrO_2$; Its molecular weight (221) is confirmed by the percentage of Br.

$$\frac{100 \times 80}{36·2} = 221.$$

The second acid.

		Per cent.	gm.atom	atomic ratio
C	$= \frac{8·552 \times 12 \times 100}{44 \times 3·4} =$	68·6	5·71	4
H	$= \frac{2·618 \times 2 \times 100}{18 \times 3·4} =$	8·55	8·55	6
O	by difference	22·85	1·43	1

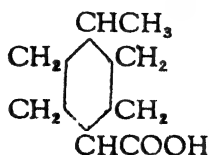
∴ The empirical formula of the second acid is C_4H_6O.

As it is an acid it must contain 2 oxygen atoms; besides it is obtained from the bromoderivative $C_8H_{13}BrO_2$.

∴ The molecular formula of this second acid is $C_8H_{12}O_2$.

The original acid is derived from *p*-xylene and its molecular formula is $C_8H_{14}O_2$.

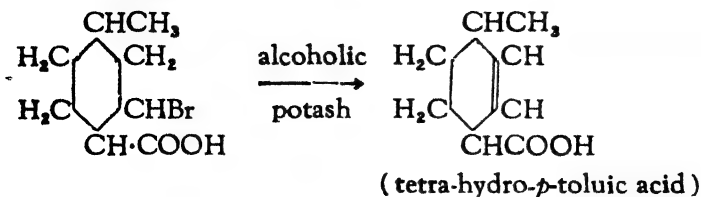
Therefore it must be

CHCH$_3$
CH$_2$ CH$_2$
CH$_2$ CH$_2$
CHCOOH

The bromoderivatative is $C_8H_{13}BrO_2$ and its structure is

CHCH$_3$
H$_2$C CH$_2$
H$_2$C CHBr
CH·COOH

$\xrightarrow[\text{potash}]{\text{alcoholic}}$

CHCH$_3$
H$_2$C CH
H$_2$C CH
CHCOOH

(tetra-hydro-*p*-toluic acid)

(27) (*a*) 0·25 gm. of a hydrocarbon gave on combustion 0·8593 gm. CO_2 and 0·1406 gm. H_2O. (*b*) When heated with conc. H_2SO_4 a monosulphonic acid was formed, 0·208 gm. of which required 2 c. c. of 0·5 N NaOH for neutralization. (*c*) The hydrocarbon when oxidised yielded a dibasic acid 0·95 gm. of the silver salt of which left on ignition a residue of 0·54 gm. silver. (*d*) The dibasic acid on heating gives an anhydride, which when heated with ammonia and then with KOH and bromine yielded a monobasic acid containing 10·22°/₀ nitrogen. Assign the structural formula to the monobasic acid mentioned in (*d*).

The empirical formula of the hydrocarbon (a)

	Per cent.	gm. atom	atomic ratio
$C = \dfrac{0{\cdot}8593 \times 12 \times 100}{44 \times 0{\cdot}25} =$	93·7	7·8	5
$H = \dfrac{0{\cdot}1406 \times 2 \times 100}{18 \times 0{\cdot}25} =$	6·3	6·3	4

The empirical formula is C_5H_4 (64)

The equivalent weight of the monosulphonic acid derived from the hydrocarbon (a) is

$$\frac{1000 \times 0{\cdot}208}{2 \times 0{\cdot}5} = 208.$$

The molecular weight of the hydrocarbon can be got by substracting SO_3 (80) from the equivalent weight of the mono-sulphonic acid 208   208 − 80 = 128.

The molecular formula of the hydrocarbon is therefore $C_{10}H_8$; it is therefore naphthalene

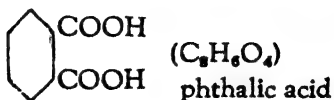
The hydrocarbon (*a*) on oxidation yields a dibasic acid (c):

The molecular wt. of the silver salt is

0·54 gm. Ag 216 : : 0·95 Ag salt : 380

∴ The mol. wt. of the dibaic acid (c) is 380 − 216 + 2 = 166.

As it is a dibasic acid, its constitution can be represented as :

COOH
COOH
($C_8H_6O_4$)
phthalic acid

∴ The molecular wt. of the monobasic acid (d) is

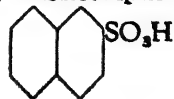
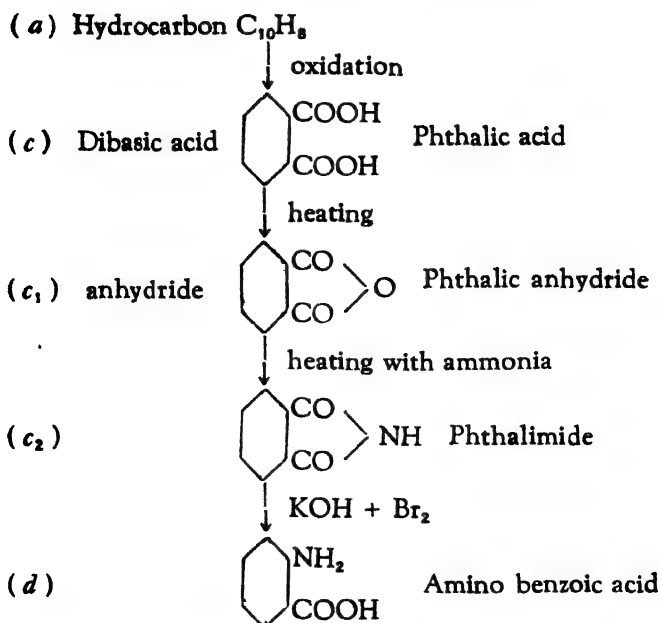
$$\frac{100 \times 1}{10{\cdot}22} = 137$$

And its structure can be represented as :

NH_2
COOH

The various reactions are as shown :—

(*a*) Hydrocarbon $C_{10}H_8$ (*b*) Monosulphonic acid

Naphthalene
Mol. wt. 166   Mol. wt. 208

(28) An organic compound (A) containing C, H, and O only and having a molecular weight between 178 and 182 (i) gives on combustion C = 66·7%; H = 6·6%; (ii) forms a phenylhydrazone containing N = 10·37% and (iii) gives on oxidation an acid (B) $C_9H_{10}O_4$ characterised by the formation of an ester which resists hydrolysis with alkali under ordinary conditions. The acid (B) on heating with soda lime gives a neutral liquid (C) [C = 69·5%, H = 7·2%] which on heating with anhydrous $AlCl_3$ gives resorcinol. Assign giving reasons the probable structure of (A), (B), and (C).

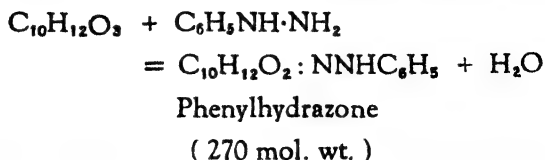
The compound (A).

(i)	Per cent.	gm. atom	atomic ratio
C	66·7	5·56	10
H	6·6	6·6	12
O by difference	26·7	1·67	3

The empirical formula $C_{10}H_{12}O_3$ of the compound is also the molecular formula as the molecular weight (180) calculated therefrom is between 178 and 182 as given.

(ii) The compound (A) forms phenylhydrazone which should have the mol. wt. 270 as the following reaction shows

$$C_{10}H_{12}O_3 + C_6H_5NH{\cdot}NH_2$$
$$= C_{10}H_{12}O_2 : NNHC_6H_5 + H_2O$$

Phenylhydrazone
(270 mol. wt.)

The molecular weight 270 is confirmed by the percentage of nitrogen.

$$\frac{100 \times 28}{10{\cdot}37} = 270.$$

The fact that the compound forms a phenylhydrazone indicates the presence of aldehyde or ketone group in the original compound.

(iii) The compound (A) gives on oxidation an acid (B) $C_9H_{10}O_4$. The acid contains less number of carbon atoms than the original substance, and eliminates the choice of aldehyde group. The original substance therefore contains a ketone group.

The acid (B) is further characterised by the formation of ester which resists hydrolysis with alkali under ordinary conditions. This means that there is steric hindrance and the two adjacent positions on either side of COOH are occupied.

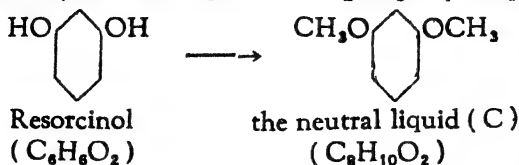
The neutral liquid (C).

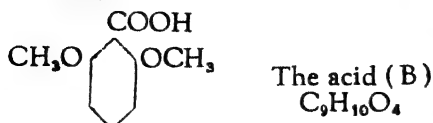
	Per cent.	gm. atom	atomic ratio
C	69·5	5·79	8
H	7·2	7·2	10
O by difference	23·3	1·45	2

The molecular formula is $C_8H_{10}O_2$. This neutral liquid on heating with anhydrous $AlCl_3$ forms resorcinol $C_6H_6O_2$; this shows that liquid is ether, and that it is methyl ether is indicated by the difference of $2CH_2$ in the molecular formula.

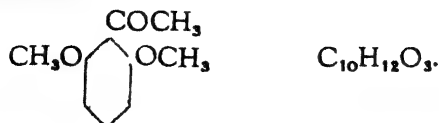
So starting from resorcinol, we get the structure of the neutral liquid by substituting H of OH groups by CH_3 groups

HO—⟨benzene ring⟩—OH ⟶ CH_3O—⟨benzene ring⟩—OCH_3

Resorcinol ($C_6H_6O_2$) — the neutral liquid (C) ($C_8H_{10}O_2$)

The neutral liquid is formed by heating the acid (B) with soda lime. This acid requires that both the adjacent positions to be occupied. The structure of the acid therefore can be constructed by putting COOH between the 2 OCH_3 groups.

COOH
CH_3O—⟨benzene ring⟩—OCH_3

The acid (B)
$C_9H_{10}O_4$

The acid (B) is formed by the oxidation of the original substance (A) which contains CO group. The structure of the original substance would be

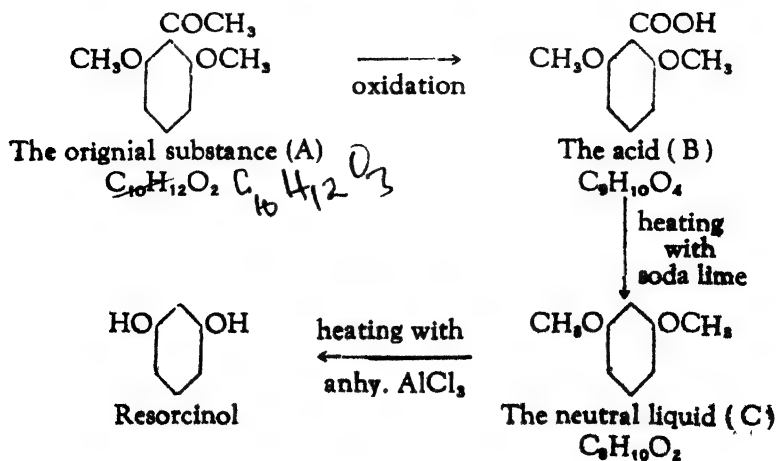
$COCH_3$
CH_3O—⟨benzene ring⟩—OCH_3 $C_{10}H_{12}O_3$.

The various reactions will be summarised as

$COCH_3$
CH_3O—⟨benzene ring⟩—OCH_3 ⟶ (oxidation) CH_3O—⟨benzene ring with COOH⟩—OCH_3

The orignial substance (A) — The acid (B)
$C_{10}H_{12}O_2$ $C_{10}H_{12}O_3$ — $C_9H_{10}O_4$

↓ heating with soda lime

HO—⟨benzene ring⟩—OH ⟵ (heating with anhy. $AlCl_3$) CH_3O—⟨benzene ring⟩—OCH_3

Resorcinol — The neutral liquid (C) $C_8H_{10}O_2$

(29) A primary amino fatty acid (A) gave a benzoyl derivative (B). 0·15 gm. of (B) yielded 10·3 c. c. of nitrogen measured over water at 20°C. and 757 mm. pressure (vapour pressure of water at 20°C = 18 mm.). The molecular weight of (B) was found to be 179. (B) when condensed with benzaldehyde gave a product (C) which was reduced to (D). (D) on hydrolysis gave an acid (E) containing C = 65·3%, H = 6·7%, N = 8·5%, the remainder being oxygen. Assign structures to compounds from (A) to (E).

The molecular weight of (B) can be calculated from the nitrogen measurements.

Percentage of Nitrogen

$$\frac{28 \times 742 \times 10{\cdot}3 \times 273 \times 100}{293 \times 760 \times 22400 \times 0{\cdot}15} = 7{\cdot}8.$$

The molecular weight of (B).

$$\frac{100 \times 14}{7{\cdot}8} = 179{\cdot}5.$$

This agrees well with the molecular weight given *i. e.* 179.

(B) is a benzoyl derivative of a primary amino acid and can be represented as

$C_6H_5CONH\ X\ COOH$, where X is the middle chain, the nature of which can be ascertained by deducting the total weight of the known atoms from the molecular weight *i. e.* 179.

$$179 - 165 = 14$$

X is therefore CH_2, and (B) becomes $C_6H_5CONHCH_2COOH$ and the primary amino acid (A) NH_2CH_2COOH.

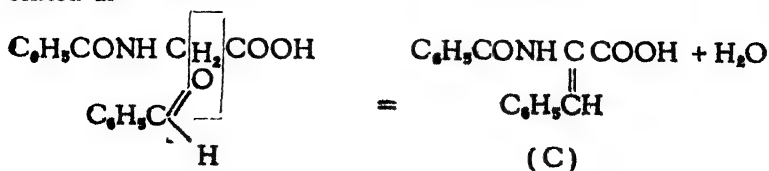
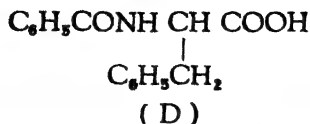
The condensation of (B) with benzaldehyde can be represented as

$$C_6H_5CONH\ C\boxed{H_2}COOH + C_6H_5C\overset{\boxed{O}}{\diagup\!\!\diagup}\!\!\diagdown H = \underset{\substack{\| \\ C_6H_5CH}}{C_6H_5CONH\ C\ COOH} + H_2O$$

(C)

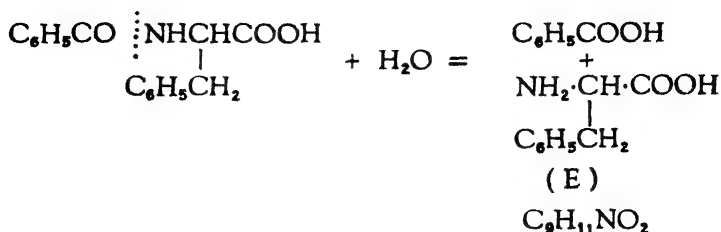
(C) on reduction will give

$$\begin{array}{c} C_6H_5CONH\ CH\ COOH \\ | \\ C_6H_5CH_2 \end{array}$$

(D)

where double bond vanishes by the introduction of 2 H atoms.

(D) on hydrolysis gives an acid containing nitrogen which means that the benzoyl group is eliminated. The resulting compound will be

$$C_6H_5CO \vdots \begin{array}{c} NHCHCOOH \\ | \\ C_6H_5CH_2 \end{array} + H_2O = \begin{array}{c} C_6H_5COOH \\ + \\ NH_2 \cdot CH \cdot COOH \\ | \\ C_6H_5CH_2 \end{array}$$

(E)

$C_9H_{11}NO_2$

The molecular formula of (E) agrees well with the analytical data.

	Per cent.	gm. atom	atomic ratio
C	65·3	5·44	9
H	6·7	6·7	11
N	8·5	0·60	1
O	19·5	1·2	2
			$C_9H_{11}NO_2$

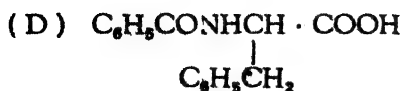
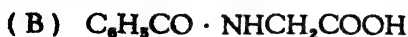
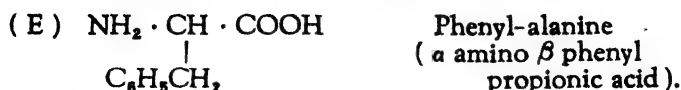
The structures of the various substances are, therefore,

(A) $NH_2 \cdot CH_2 \cdot COOH$

(B) $C_6H_5CO \cdot NHCH_2COOH$

(C) $\begin{array}{c} C_6H_5CONHC \cdot COOH \\ \| \\ C_6H_5CH \end{array}$

(D) $\begin{array}{c} C_6H_5CONHCH \cdot COOH \\ | \\ C_6H_5CH_2 \end{array}$

(E) $NH_2 \cdot CH \cdot COOH$ with $C_6H_5CH_2$ attached to the CH — Phenyl-alanine (α amino β phenyl propionic acid).

(30) 0·138 gm. of an organic acid (A) is neutralised by 10·0 c. c. of N/10 alkali. With acetic anhydride it yields a compound (H) containing 60·00 per cent. carbon, 4·44 per cent. hydrogen and 35·56 per cent. oxygen.

Another substance (B) obtained by the action bromine on benzoic acid contains 39·8 per cent. halogen and on fusion with alkali yields, a product isomeric with (A). Upon nitration, B yields two isomeric substances (C) and (D) containing 5·6 per cent. nitrogen, but both of these reduce to the same halogen-free product (E). Diazotization and boiling with water converts (E) to (F) (Salicylic acid) which is also isomeric with A.

Assign a structure to (A).

The empirical formula of the compound (H) can found from the percentages of the elements which are C, H and O only

	per cent.	gm. atom	atomic ratio
C	60·00	5·00	9
H	4·44	4·44	8
O	35·56	2·22	4

The empirical formula of the compound (H) is $C_9H_8O_4$, and that of (A) ($C_9H_8O_4$ − $OCCH_3$ + H) $C_7H_6O_3$ (138) which agrees well with the equivalent weight

$$\frac{0{\cdot}138 \times 10000}{10} = 138.$$

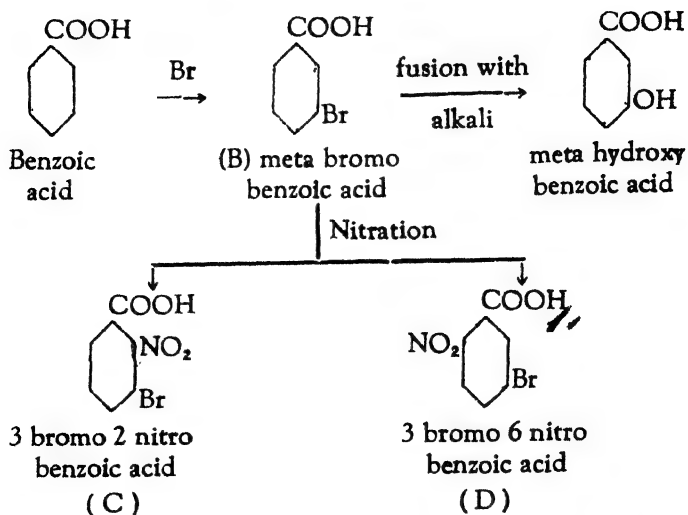
The substance (B) obtained by the action of bromine on benzoic acid C_6H_5COOH (122 mol. wt.) contains 39·8 per cent. halogen; that means it is a mono bromo benzoic acid $C_6H_4BrCOOH$ which contains $\frac{80 \times 100}{201} = 39{\cdot}8$ per cent. bromine. The bromine atom occupies the meta position, because it is then only possible to get two nitro compounds (C) and (D) which will on reduction give only one halogen free substance

(E). The compound (C) and (D) contain only one NO_2 group, this is confirmed by the percentage of nitrogen :

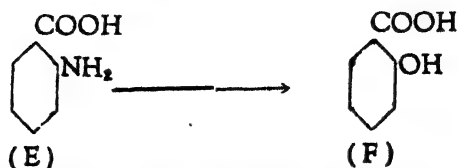
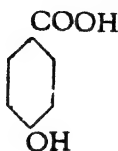
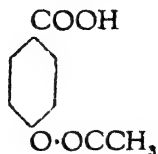
$$\frac{14 \times 100}{247} = 5{\cdot}66.$$

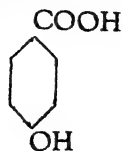
Compounds (C) and (D)

$C_6H_3Br{\cdot}NO_2COOH$.

The various reactions involved can be represented as

The substances (C) and (D) will be reduced to only one halogen-free amino acid *i. e.* ortho amino benzoic acid which on diazotization and boiling with water gives ortho hydroxy benzoic acid (F) *i. e.* salicylic acid.

COOH, NH_2 ⟶ COOH, OH

(E) (F)

This ortho acid, and the meta acid found by the fusion of (B) with alkali are isomeric with the acid (A) which is therefore para hydroxy benzoic acid,

whose equivalent weight is 138. This will react with acetic anhydride and will form a phenolic ester

having the molecular formula $C_9H_8O_4$ which agrees well with the analysis.

The organic acid (A) is therefore para-hydroxy-benzoic acid

CHAPTER III

PROBLEMS FOR SOLUTION

(31) A substance containing carbon, hydrogen and oxygen gave on combustion the following results : Substance, 0·32 gm.; CO_2, 0·44 gm.; H_2O, 0·36 gm. What is the simplest formula for the substance ?

Ans. : CH_4O.

(32) If 0·360 gram of an organic compound which contains only carbon, hydrogen and oxygen yields on combustion 0·528 gram of carbon dioxide and 0·216 gram water, what is the empirical formula ?

Ans. : CH_2O.

(33) A substance containing only carbon, hydrogen and oxygen was found on analysis to contain C = 52·15, H = 13·1 per cent.; a vapour density determination gave D = 23. Determine the molecular formula of the substance.

Ans. : C_2H_6O.

(34) 0·37 gram of a substance containing carbon, hydrogen and oxygen gave on combustion 0·66 gram CO_2 and 0·27 gm. water. Further 0·123 gram of the substance displaced 39·6 c. c. of air at 17° C. and 760 mm. in a determination of its vapour density by the Victor Meyer method. Assign from these data the molecular formula of the substance.

Ans. : $C_3H_6O_2$.

(35) A liquid containing C, H and O gave on analysis the following results ; 0·1746 gram gave 0·3492 gram carbon dioxide and 0·1426 gram water. The vapour density of the substance was found to be 22 (H = 1.). Find the formula of the liquid.

Ans. : C_2H_4O.

(36) The analysis of an organic substance gave the following results : 0·2115 gram on complete combustion gave 0·4655 gram carbon dioxide and 0·2533 gram of water. The vapour density of the substance was 29·7. Calculate the molecular formula, and give the names of the substances possessing this formula.

Ans. : C_3H_8O (Propyl alcohol. Iso-propyl alcohol, Methyl ethyl ether).

(37) 0·1027 gram of a substance gave on combustion 0·2178 gram CO_2 and 0·0303 gram H_2O. 0·1130 gram gave 0·0643 gram AgBr. What is the simplest possible empirical formula of the substance ?

Ans. : $C_{16}H_{11}O_3$ Br.

(38) A substance gave the following results on analysis :—

(*a*) 0·1836 gram gave by combustion 0·1934 gram of CO_2 and 0·0693 gram of H_2O.

(*b*) 0·3212 gram gave 0·3616 gram AgBr.

What is the simplest formula for this substance ?

Ans. : $C_4H_7O_2Br$.

(39) A dibasic acid containing only carbon, hydrogen and oxygen was found by analysis to contain C = 26·7°/₀, H = 2·2°/₀.

A determination of the vapour density of its methyl ester gave Δ = 59. What is the acid ?

Ans. : $C_2H_2O_4$ oxalic, acid.

(40) A substance gave the following results on analysis :—

0·2500 gram gave 0·6027 gram CO_2 and 0·339 gram H_2O.

0·2000 gram gave 33·4 c.c. of nitrogen at 20°C. and 750 mm.

Its vapour density compared with hydrogen was 37. Calculate the composition of the substance and give the constitutional formulæ of the possible substances of this composition.

Ans. : $C_4H_{11}N$.

(i) $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$.

(ii) $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH \cdot CH_2 \cdot NH_2.$

(iii) $\begin{matrix}CH_3\\CH_3-\\CH_3\end{matrix}\!>\!C \cdot NH_2.$

(iv) $\begin{matrix}CH_3 \cdot CH_2\\CH_3\end{matrix}\!>\!CH \cdot NH_2.$

(v) $\begin{matrix}CH_3 \cdot CH_2 \cdot CH_2\\CH_3\end{matrix}\!>\!NH.$

(vi) $\begin{matrix}CH_3 \cdot CH_2\\CH_3 \cdot CH_2\end{matrix}\!>\!NH.$

(vii) $\begin{matrix}\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\\CH_3\end{matrix}\!>\!NH.$

(viii) $\begin{matrix}C_2H_5\\CH_3-\\CH_3\end{matrix}\!>\!N.$

(41) A ketoxime on analysis, was found to possess the following composition :—

Carbon 55·2, hydrogen 10·3, nitrogen 16·1 per cent. What is the formula of this compound and from what ketone is it derived ?

Ans. : $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!C : N \cdot N \cdot OH$ from methyl ethyl ketone.

(42) A substance gave the following results on analysis

(*a*) 0·1836 gram gave, on combustion, 0·2241 gram CO_2 and 0·0420 gram of H_2O.

(*b*) 0·3212 gram gave 0·3736 gram of AgBr.

What is the simplest possible formula for the substance ?

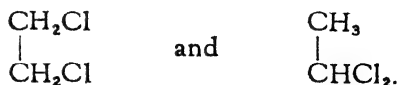
Ans : $C_9H_8O_3Br_2$.

(43) Two liquids, one boiling at 83°C and the other at 57°C gave on analysis the same results, viz. 0·2376 gram gave, on combustion, 0·2112 gram CO_2 and 0·0864 gram H_2O ; 0·121 gram gave, when heated with silver nitrate and nitric acid, 0·351 gram AgCl. Calculate the simplest formula for these substances. How do you account for two substances having the same composition, and what do you regard as the true formula of each compound ?

Ans. : Empirical formula CH_2Cl,

CH_2Cl
|
CH_2Cl

and

CH_3
|
$CHCl_2$.

(44) A substance gave the following results on analysis :— 0·197 gram gave 0·293 gram CO_2 and 0·150 gram H_2O.

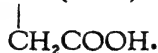
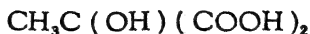
By the Kjeldahl method 0·59 gram required 10 c. c. of N H_2SO_4 for neutralisation of the ammonia. The original substance when boiled with caustic soda, evolved ammonia and the dry residue heated with soda lime, gave off methane. What is the substance ?

Ans. : CH_3CONH_2, Acetamide.

(45) Calculate the formula of the aliphatic dicarboxylic acid which gave the following results on analysis :—

0·1340 gram gave 0·1760 gram CO_2 and 0·0540 gram H_2O.

Ans. : CH (OH) COOH
|
CH_2COOH. — Malic acid

$CH_3C (OH) (COOH)_2$ — Isomalic acid

$CH_2 (OH) CH (COOH)_2$ — β–hydroxy iso-succinic acid.

(46) 0·2543 gram of a liquid hydrocarbon gave on combustion 0·8513 gram CO_2 and 0·1991 gram H_2O ; a vapour density determination gave D = 46. Find its empirical formula. The hydrocarbon on oxidation gave an acid of the empirical formula $C_7H_6O_2$. Find the structural formula of the hydrocarbon.

Ans. : $C_6H_5CH_3$.

(47) The combustion of 0·246 gram of a liquid hydrocarbon yielded 0·792 gram of carbon dioxide and 0·270 gram of water. The hydrocarbon absorbed bromine readily, and yielded, a compound containing 79·6 per cent. of bromine. From these data what conclusions do you draw as to the formula of the hydrocarbon ?

Ans. : C_6H_{10} A doubly unsaturated aliphatic hydrocarbon.

(48) 0·2 gram of an anhydrous acid gave on combustion, 0·040 gram H_2O and 0·195 gram CO_2. The acid is found to be dibasic, and 0·5 gram of the silver salt leaves, on ignition, 0·355 gram silver. What is the simplest formula for the acid, and what is its molecular formula ?

Ans. : CHO_2, $C_2H_2O_4$.

(49) A mono–acid organic base gave the following results on analysis :—

0·100 gram gave 0·2882 gram CO_2 and 0·0756 gram water. 0 200 gram gave 21·8 c.c. nitrogen at 15°C and 760 mm. pressure. 0·400 gram of the platinichloride left on ignition 0 125 gram of platinum.

What is the molecular formula of the base ?

Ans. : C_7H_9N.

(50) Certain white crystals having, in aqueous solution, a strongly acid reaction were found to consist of H = 4·76, C = 19·05, O = 76·19 per cent. What is the simplest formula which would express the results of the analysis ? Is the formula adopted for the compound ? If not, why ?

Ans. : CH_3O_3 : The compound is $(COOH)_2$, $2H_2O$.

(51) A hydrocarbon of the formula C_8H_{10} yields on oxidation, a colourless crystalline dibasic acid, containing 57·8 per cent. of carbon, 3·6 per cent. of hydrogen. The silver salt contains 56·8 per cent. silver. On heating the acid it is converted into a compound of the formula $C_8H_4O_3$. On distillation with lime, benzene is formed. Discuss the structure of the original hydrocarbon.

Ans. : *o*–Xylene $C_6H_4(CH_3)_2$.

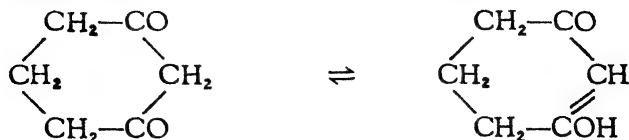
(52) The monocyclic carbon compound (A) containing only carbon, hydrogen and oxygen gave the following results on analysis : 0·1120 g. gave 0·2638 g. CO_2 and 0·0720 g. H_2O. When heated with ethyl alcohol and 5 per cent. sulphuric acid, (A) was converted into a substance containing C = 68·46, H = 8·67 per cent.

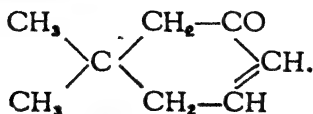
When (A) was heated with bromine in chloroform solution, bromine was absorbed, hydrogen bromide evolved, and a compound produced containing Br = 41·78 per cent. With hydroxylamine hydrochloride (A) gave a substance containing N = 19·84 per cent.

What information can you deduce from these data regarding the presence of any particular groupings in (A), and what formula can you suggest which would be in accord with the observed facts ?

Ans. The simplest formula C_3H_4O.
The bromine derivative $C_6H_7BrO_2$.
The ethyl ether $C_6H_7(C_2H_5)O_2$.
The dioxime $C_6H_8(N{\cdot}OH)_2$.

The formation of ether indicates the presence of — OH group, and the formation of dioxime, the presence of two ketone groups and (A) can be represented as

```
   CH2—CO                     CH2—CO
  /      \                   /      \
CH2       CH2      ⇌       CH2       CH
  \      /                   \      //
   CH2—CO                     CH2—COH
```

(53) A substance of the formula

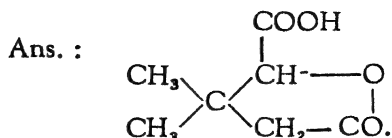
```
CH3       CH2—CO
   \     /      \
    >C<          >CH.
   /     \      //
CH3       CH2—CH
```

on oxidation with potassium permanganate gave a product which was analysed with the following results :—

0·111 g. gave 0·2142 g. CO_2 and 0·0654 g. H_2O.

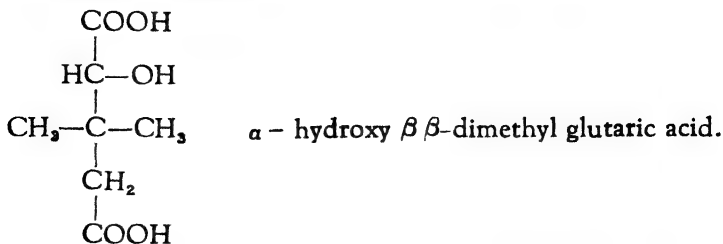
0·2019 required 12·85 c. c. $\frac{N}{10}$ sodium hydroxide for neutralisation in the cold and a further 11·9 c.c. on warming.

What structural formula would you assign to this oxidation product ?

Ans. :

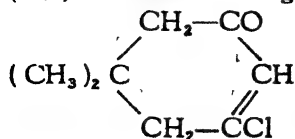
```
              COOH
               |
CH3\         /CH——O
     >C<          |
CH3/         \CH2—CO.
```

Lactone of α-hydroxy β β-dimethyl glutaric acid.

On warming the glutaric acid is formed thus requiring further amount of alkali for neutralisation.

```
      COOH
       |
      HC—OH
       |
CH3—C—CH3        α - hydroxy β β-dimethyl glutaric acid.
       |
      CH2
       |
      COOH
```

(54) The ammonium salt of a non-nitrogenous organic acid gave the following results on analysis : 0·2856 gram gave 0·3102 gram CO_2 and 0·180 gram H_2O and 0·1562 gram gave 22·1 c.c. of dry nitrogen at 13°C. and 779 mm. pressure. Find the simplest formula for the salt and for the acid.

Ans. : salt, $C_6H_{17}O_7N_3$; and acid, $C_6H_8O_7$ or $C_3H_5O\,(COOH)_3$
i. e. Citric acid or an isomer.

(55) A ketone having the formula

```
          CH2—CO
         /       \
(CH3)2 C          CH
         \       //
          CH2—CCl
```

was reduced by means of sodium in absolute alcoholic solution ; 0·1499 gram of the resulting compound (A) gave, on

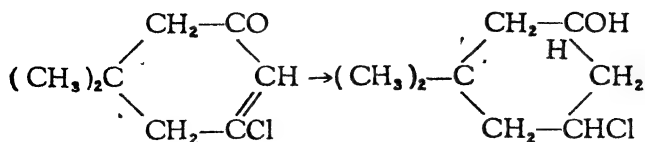
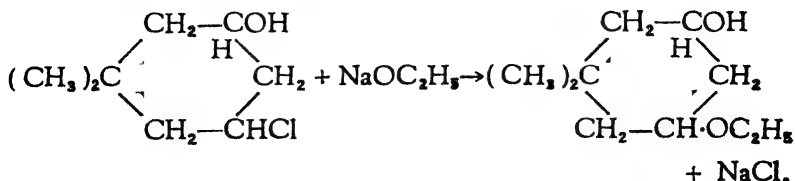
combustion, 0·3835 gram CO_2 and 0·1559 gram H_2O. When treated with benzoyl chloride, (A) was converted into a substance (B) which contained 73·75 per cent. of carbon and 8·85 percent of hydrogen. What are the most probable formulæ for (A) and (B) ? Explain the reactions by which they are produced.

Ans. : The reduction by means of sodium in absolute alcohol is accompanied by ether formation. Though the two processes take place simultaneously, they can be represented in two stages as follows :—

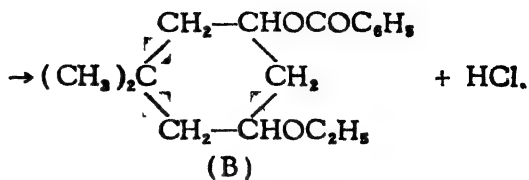
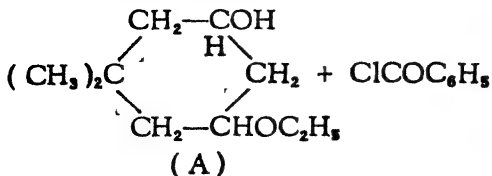
(i) Reduction proper

```
         CH2—CO                          CH2—COH
        /       \                       /    H\
( CH3 )2C        CH →( CH3 )2—C              CH2
        \       //                      \     /
         CH2—CCl                         CH2—CHCl
```

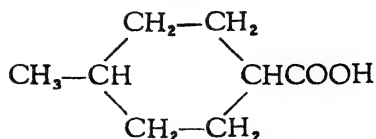
(ii) Ether formation

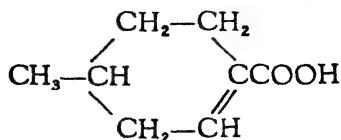
```
         CH2—COH                                     CH2—COH
        /    H\                                     /    H\
( CH3 )2C       CH2 + NaOC2H5→( CH3 )2C               CH2
        \      /                                    \     /
         CH2—CHCl                                    CH2—CH·OC2H5
                                                           + NaCl.
```

When (A) is treated with benzoyl chloride, an ester of benzoic acid is formed with the evolution of hydrochloric acid.

```
         CH2—COH
        /    H\
( CH3 )2C       CH2 + ClCOC6H5
        \      /
         CH2—CHOC2H5
            ( A )

                       CH2—CHOCOC6H5
                      /      \
           → ( CH3 )2C        CH2          + HCl.
                      \      /
                       CH2—CHOC2H5
                          ( B )
```

(56) An acid derived from *p*-xylene, gave the following results on analysis : 0·162 gram gave 0·4015 gram CO_2 and 0·1430 gram H_2O. When treated with bromine, it was converted into a bromo derivative containg 36·2 per cent. of bromine and this, when digested with alcoholic potash yielded an acid which gave the following results on analysis : 0·17 gram gave 0·4276 gram CO_2 and 0·1309 gram H_2O. Assign constitutional formulæ to these acids, stating your reasons for their selection.

Ans. :

```
              CH2—CH2
             /       \
    CH3—CH            CHCOOH
             \       /
              CH2—CH2
```

This formula agrees well with the molecular weight calculated from the bromine percentage of the bromoderivative. The other acid is

```
              CH2—CH2
             /       \
    CH3—CH            CCOOH
             \       //
              CH2—CH
```

(57) A dibasic acid gave on analysis, the following results : 0·1740 gram gave 0·3388 gram CO_2 and 0·1008 gram H_2O. When it was treated with bromine, it yielded a dibromo derivative which gave on analysis C = 26·4, H = 3·2 and Br = 50·3 per cent. Oxidation with permanganate converted the dibasic acid into dimethyl malonic acid and oxalic acid. What is the constitution of the acid ?

Ans. : α, α–dimethyl glutaconic acid
$COOH{\cdot}C(CH_3)_2\,CH : CH\,(COOH)$.

(58) An organic acid gave the following results on analysis : 0·1792 gram gave 0·3826 gram CO_2 and 0·1370 gram H_2O. The silver salt contained 43·0 per cent. of silver, and oxime contained 8·8 per cent. of nitrogen. What constitutional formulæ may the acid have ?

Ans. : $CH_3(CH_2)_3\,CO{-}CH_2{\cdot}COOH$.
or
$CHO \cdot (CH_2)_5\,COOH$.

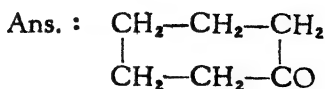
(59) An organic acid gave the following results on analysis: 0·1531 gram gave 0·3883 gram of carbon dioxide and 0·1410 gram of water. The silver salt gave 41·1 per cent. of silver, and when the acid was treated with bromine and afterwards with alcoholic potash it gave an acid containing 70·1 per cent. of carbon and 9·1 per cent. of hydrogen. The latter on heating with sulphuric acid was converted into an aromatic acid which yielded *m*–xylene on distillation with lime. Suggest formulae for the three acids.

Ans. : The first acid : $(CH_3)_2C_6H_9COOH$.
Hexa hydro dimethyl benzoic acid.

The second acid : $(CH_3)_2C_6H_7COOH$.
Tetra hydro dimethyl benzoic acid.

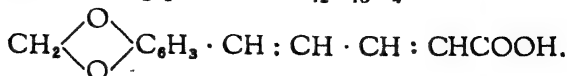
The third acid : $(CH_3)_2C_6H_3COOH$.
Dimethyl benzoic acid.

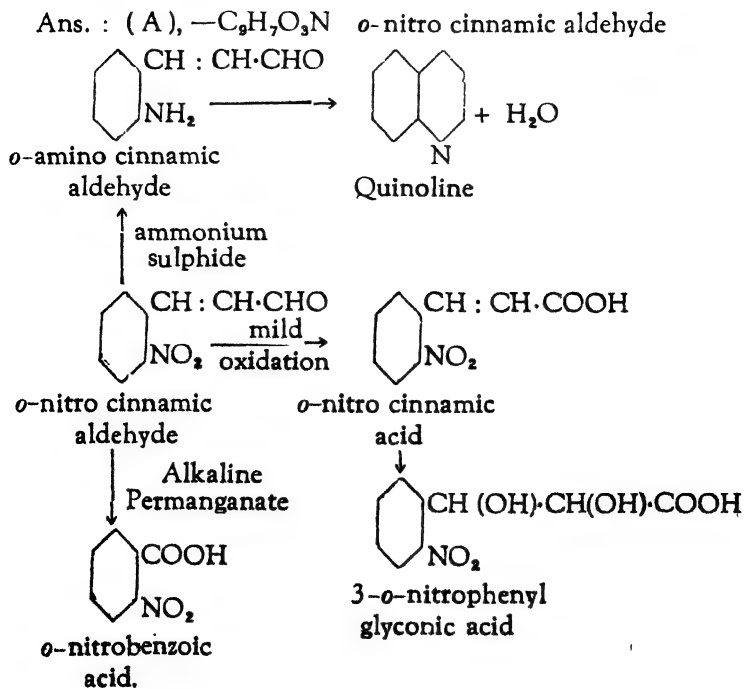
(60) The ethyl ester of a dibasic acid, to which a normal carbon chain is assigned, has the composition: C = 61·11; H = 9·26; and O = 29 63 per cent. When heated at 120° with sodium and a trace of alcohol this ester is converted into a substance A of the composition: C = 63·53, H = 8·23; O = 28·24 per cent. From A, when boiled with dilute sulphuric acid, a second substance B is obtained of the composition: C = 73·47; H = 10·20; O = 16·33 per cent., the oxime of which contains N = 12·39 per cent. What is the probable constitution of B?

Ans. :
```
CH2—CH2—CH2
|        |
CH2—CH2—CO
```

(61) A monobasic organic acid A gave the following results on analysis. 0·1430 gram gave 0·3465 gram CO_2 and 0·0592 gram H_2O; 0·3819 gram required 17·55 c. c. $\frac{N}{10}$ NaOH for exact neutralisation. On treatment with bromine A gave a compound which was analysed with the following results: 0·1821 gram gave 0·1787 gram CO_2 and 0·0304 gram H_2O; 0·1520 gram gave 0·2124

gram AgBr and M. W. = 540. Oxidation of A gave first a compound of the formula $C_8H_6O_3$ and subsequently $C_8H_6O_4$ which on heating with hydrochloric acid yielded 3:4–Dihydroxy-benzoic acid. Assign a structure to the acid A.

Ans. : A is piperic acid–$C_{12}H_{10}O_4$.

$$CH_2\langle{}^{O}_{O}\rangle C_6H_3 \cdot CH : CH \cdot CH : CHCOOH.$$

(62) An organic compound (A) of M. W. 177 containing C, 61·0°/₀ ; H, 3·9 %; O, 27·1°/₀ and N, 7·9°/₀ on mild oxidation gave a compound of the formula $C_9H_7O_4N$ which with dilute acid potassium permanganate gave a product of the formula $C_7H_5O_4N$ and (A) on reduction with ammonium sulphide gave a compound which loses one molecule of water to give quinoline. Indicate the structure of (A) and the cause of the reactions described above.

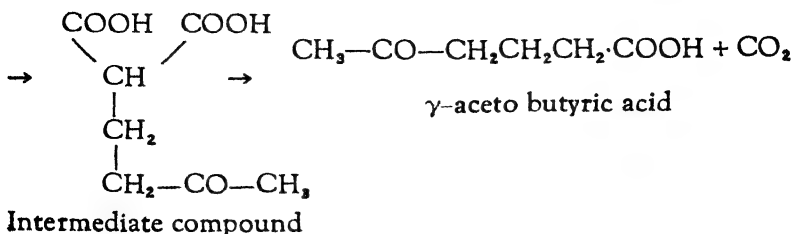
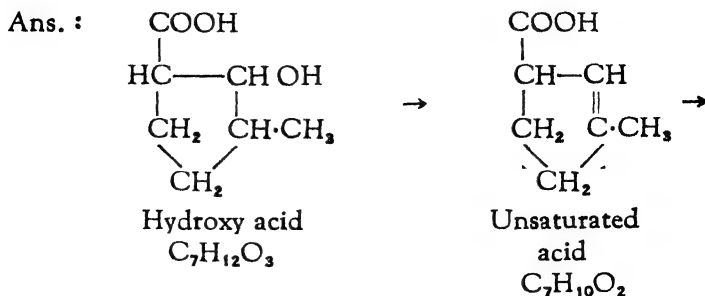
Ans. : (A), —$C_9H_7O_3N$ *o*-nitro cinnamic aldehyde

(63) A cyclic hydroxy-monobasic acid yielded on analysis the following results :—

0·1800 g. gave 0·3854 g. CO_2 and 0·1346 g. H_2O. When this acid was treated with dehydrating agents an unsaturated acid was obtained which gave on analysis, C, 66·7°/₀; H, 7·9%. The latter on oxidation gave γ-aceto-butyric acid. Discuss the constitution of the hydroxy acid and the unsaturated acid.

Ans. :

→ $(COOH)_2CH—CH_2—CH_2—CO—CH_3$ → $CH_3—CO—CH_2CH_2CH_2·COOH + CO_2$

Intermediate compound

γ-aceto butyric acid

(64) Two isomeric substances A and B gave the following results on analysis :—

0·197 g. gave 0·293 g. CO_2 and 0·150 g. H_2O. By Kjeldahl method 0·59 g. required 10·0 c. c. of N H_2SO_4 for neutralisation of ammonia. The substance A when boiled with caustic soda evolved ammonia and the dry residue heated with soda lime gave off methane. The substance B on reduction gave ethyl amine. Give the structural formulae of the two substances.

Ans. : A — CH_3CONH_2, Acetamide.

B — $CH_3CH : NOH$, Acetaldoxime.

(65) An organic compound (0·1438 g.) gave on combustion 0·3616 g. CO_2 and 0·0522 g. H_2O. By the Dumas method 0·1836 g. gave 6·9 c.c. of nitrogen at N.T.P. A Carius estimation on 0·2490 g. gave 0·1201 g. AgCl.

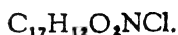
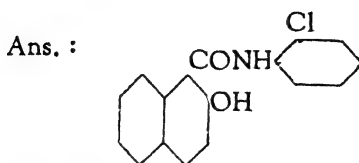
The substance was soluble in aqueous NaOH and the solution yielded a red dye with diazo-benzene chloride. By hydrolysis with strong acid or alkali under pressure the original substance gave an acid (I) and a primary amine (II). When (II) was diazotised and boiled with absolute alcohol, the product was chlorobenzene. Distillation of (I) with soda lime gave β–naphthol and an alcoholic solution of (I) exhibited an intense colour with ferric chloride ($FeCl_3$). Discuss the constitution of the substance and outline its method of preparation.

Ans. :

Cl

CONH

OH

$C_{17}H_{12}O_2NCl$.

(66) An organic compound (A) containing 92·32% C and 7·68% H and having a vapour density 39 was condensed with a second organic compound (B) containing 14·1% C ; 2·35% H and 83·55% Cl in the presence of aluminium chloride ($AlCl_3$). The vapour density of (B) was 42·5. The condensation product (C) reacted with bromine to yield a compound (D) containing 32·35% bromine. The compound (D) when heated with water to about 150° C, is changed to (E) which contains 84·8% C, 6·54% H and 8·66% O. Assign structural formulæ to compounds from (A) to (E).

Ans. : (A) C_6H_6.

(B) CH_2Cl_2.

(C) $C_6H_5—CH_2—C_6H_5$

(D) $C_6H_5—CHBr—C_6H_5$

(E) $C_6H_5—CH (OH)—C_6H_5$.

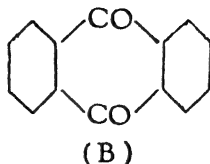
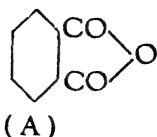
(67) An unsaturated ketone gave the following results : 0·1633 g. gave 0·44 g. CO_2 and 0·15 g. H_2O. 1·96 g. of the ketone on treatment with an excess of HCN gave 2·50 g. of the cyanhydrin. When oxidised with $KMnO_4$ solution, the ketone gave another ketone and a ketonic acid which readily yielded on oxidation CO_2 and acetic acid. Assign a structural formula to the ketone.

Ans. : $(CH_3)_2C{=}CHCO\,CH_3$, Mesityl oxide.

(68) 0·100 g. of an aromatic anhydride (A) gave on combustion 0·234 g. CO_2 and 0·024 g. H_2O. (A) was condensed with benzene in the presence of anhydrous aluminium chloride ($AlCl_3$) producing a substance (B) which on treatment with phenylhydrazine gave a hydrazone containing 14·43 per cent. N. Action of bromine on (B) gave a dibromo derivative which on fusion with KOH gave alizarin. Assign structural formula to (A) and (B).

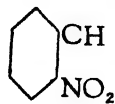
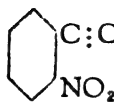
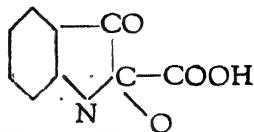
Ans. :

$C_6H_4\langle{}^{CO}_{CO}\rangle O$ (A)

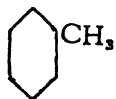
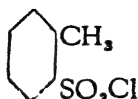
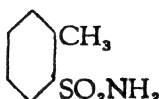
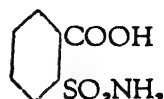
$C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_4$ (B)

(69) An aromatic acid (A) gave the following results on analysis :—0·327 gm. gave 0·671 gm. CO_2 and 0·106 gm. H_2O. 0·375 gm. gave 25·59 c. c. nitrogen at 30°C and 710 m. m. pressure. 0·400 gm. of the silver salt left a residue of 0·144 gm. silver.

When treated with bromine and caustic potash the acid (A) gave another acid (B) which contained 56·52°/₀ carbon, 2·62°/₀ hydrogen and 7·34°/₀ nitrogen. Under the influence of alkali, the acid (B) undergoes isomeric transformation and produces a third acid (C) which in its turn yields isatin by the loss of a molecule of CO_2.

Suggest constitutional formulæ for the acids, (A), (B), and (C).

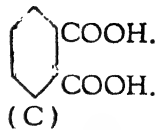
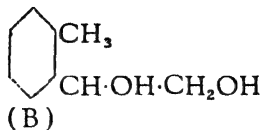
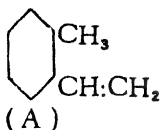
Ans. :

C_6H_4(CH : CH·COOH)(NO_2) (A) Ortho-nitro-cinnamic acid

C_6H_4(C ⋮ C·COOH)(NO_2) (B) Ortho-nitro phenyl-propiolic acid

C_6H_4(—CO—C(COOH)=N→O) (C) Isatogenic acid

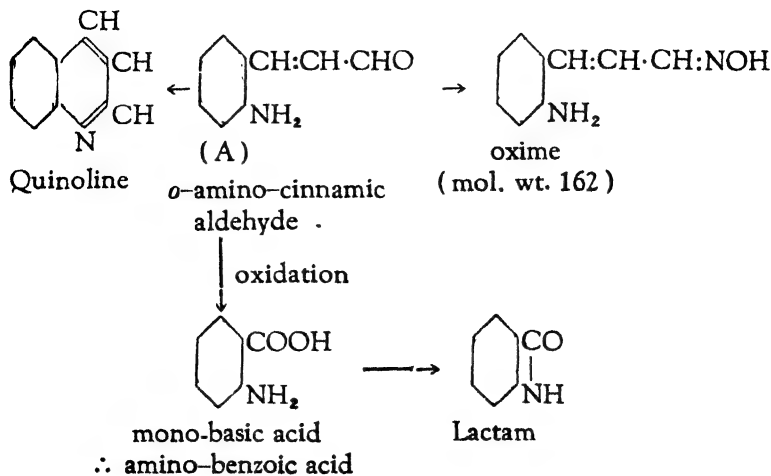
✓(70) An aromatic hydrocarbon (A) is found to have 91·37°/₀ C ; and 8·7°/₀ H. On treatment with HCl gas and SO_3 a compound (B) is formed having 44·1°/₀ C ; 3·68°/₀ H ;16·8% S ; and 18·6°/₀ Cl. (B) is treated with ammonia and a compound (C) is obtained which has 48 8°/₀ C; 5·3°/₀ H; 18·6% S and 8·1% N. The compound (C) when oxidised yields an acid (D) having 41·6% C ; 4·0% H ; 15·8% S ; and 6·9% N. (D) loses a molecule of water and yields saccharine. Assign structural formulæ to (A), (B), (C), and (D).

Ans. :

(71) A hydrocarbon (A) containing C = 91·5% and H = 8·5% the vapour density of which is 59 gives on treatment with dilute alkline $KMnO_4$ a dihydroxy derivative (B) containing C = 71% and H = 7·9%. The compound (B) on vigorous oxidation with acid $KMnO_4$ yields a dibasic acid (C) containing C = 57·84%, H 3·6%. 0·83 gm. of the acid requires 10 c. c. N NaOH for neutralisation.

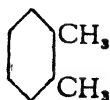
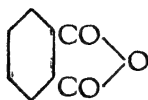
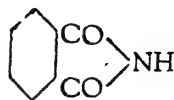
The acid (C) on heating forms an anhydride and on distilling with lime gives C_6H_6. Assign structural formulae to A, B, and C.

Ans. :

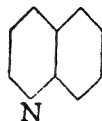
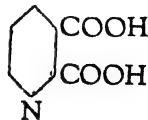
$C_6H_4(CH_3)(CH{:}CH_2)$ (A) $C_6H_4(CH_3)(CH{\cdot}OH{\cdot}CH_2OH)$ (B) $C_6H_4(COOH)(COOH)$ (C)

(72) An aromatic compound (A) gave the following results on analysis :— 0·294 gm. gave 0·792 gm. CO_2 and 0·162 gm. water : 0·200 gm. requires 13·62 $N/_{10}$ H_2SO_4 for neutralisation of the ammonia in the Kjeldahl method. (A) gives an oxime which contains 17·28% nitrogen. On oxidation (A) gives a monobasic acid which contains C = 61·4% ; H = 5·1% and N = 10·2%. The acid gives a lactam having C = 70·5% ; H = 4·2% ; N = 11·8%. The original compound (A) gives on dehydration a heterocyclic compound containing C = 83·7% ; H = 5·4°/₀ ; N = 10·9°/₀. Assign structural formulæ to (A) and its derivatives.

Ans. : The structural formula of A, with a short summary of the reactions is given below :—

(73) An organic compound of the formula C_8H_{10} (A) gave on oxidation a dibasic acid (C = 57·8°/₀ ; H = 3·6°/₀) ; the silver salt of which contained 56·8°/₀ of Ag. On heating, it gave a substance $C_8H_4O_3$ (B) which reacted with fused $(NH_4)_2CO_3$

to give a substance $C_8H_5O_2N$ (C). This substance formed a K-derivative with alcoholic caustic potash. (C) was converted by NaOCl into a substance which reacted with HNO_2 to give salicylic acid. What were the substances (A), (B) and (C) ?

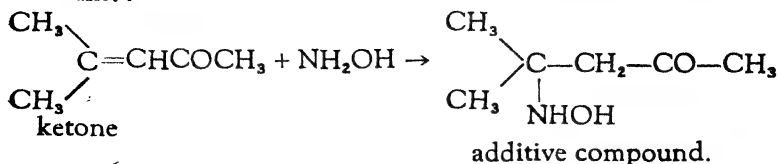
Ans. :

Ortho-xylene ; Phthalic anhydride ; Phthalimide.

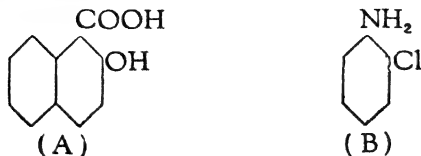
(74) A heterocyclic compound (A) having a vapour density 64, gave the following results on analysis :—0·213 gm. gave 0·654 gm. CO_2 and 0·104 gm. H_2O. 0·293 gm. gave 25·43 c.c. Nitrogen at 0°C and 760 m.m. pressure. On oxidation (A) gives a dibasic acid (B) having C = 50·3% ; H = 3·0% ; N = 8·4%. which on heating gives a second acid (C) [C = 58·5% ; H = 4·1% ; N = 11·4%]. The acid C on heating with soda lime gives a heterocyclic compound (D) having the following composition, C = 76% ; H = 6·3% ; N = 17·7 ;. Assign the structural formulæ to (A) to (D).

Ans. : The structural formulae of the compounds (A) to (D) with important reactions are given below :—

(75) An unsaturated ketone gave the following results on analysis :—0·2000 gm. gave 0·5368 gm. CO_2 and 0·1830 gm. H_2O. When oxidised with $KMnO_4$ solution the ketone gave acetone and a ketonic acid, which readily yielded on oxidation CO_2 and a monobasic acid (equivalent wt. = 60). On treatment with NH_2OH in alkaline solution, the ketone gave a compound having $C_6H_{13}O_2N$ as the molecular formula. Assign a structural formula to the product obtained, by the action of NH_2OH. upon the ketone.

Ans.:

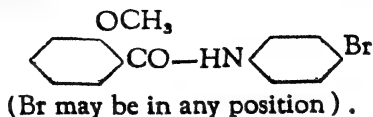
$$(CH_3)_2C{=}CHCOCH_3 + NH_2OH \rightarrow (CH_3)_2C(NHOH){-}CH_2{-}CO{-}CH_3$$

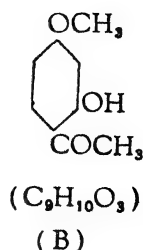
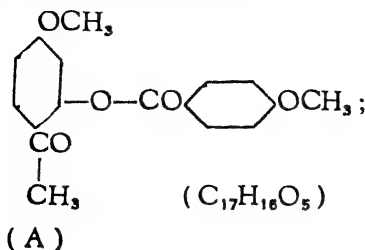
ketone — additive compound.

(76) 0·2876 gm. of an organic compound gave on combustion 0·7232 gm. CO_2 and 0·1044 gm. H_2O. and 0·1836 gm. gave 6·9 c.c. of N_2 at N. T. P. and 0·0889 gm. silver chloride. The substance was soluble in aqueous caustic soda and hydrolysed with strong acid or alkali under pressure giving an acid (A) and a primary amine (B). When (B) was diazotised and boiled with absolute alcohol the product was chlorbenzene. Distillation of (A) with soda lime gave β—naphthol. Deduce the constitution of the substances (A) and (B).

Ans.:

(77) A neutral organic substance $C_{14}H_{12}O_2NBr$ when heated with a mineral acid gives an acid $C_8H_8O_3$ (A) and a base C_6H_6NBr (B). When (A) is heated with HI, salicylic acid is produced. When (B) is diazotised and warmed with absolute alcohol, it yields bromobenzene. Give the probable constitution of the neutral substance.

Ans.:

$$C_6H_4(OCH_3){-}CO{-}HN{-}C_6H_4Br$$

(Br may be in any position).

(78) An organic compound (A) contains C = 68 00% ; H = 5·33% and – OCH_3 = 20·66%. On hydrolysis with a strong solution of caustic soda, [(A) yields *p*-methoxy benzoic acid and a phenolic ketone (B) having the formula $C_9H_{10}O_3$. The ethyl ether of (B) when heated with sodium hypochlorite gave chloroform, and 2-ethoxy 4 methoxy benzoic acid. Assign structural formulæ to (A) and (B).

Ans. : The structural formulæ of the compounds (A) and (B) are as given below :—

OCH_3 (ring) —O—CO—(ring)—OCH_3 ; with CO—CH_3 on the first ring

($C_{17}H_{16}O_5$)

(A)

OCH_3 (ring) OH, $COCH_3$

($C_9H_{10}O_3$)

(B)

PROBLEMS IN PHYSICAL CHEMISTRY

FOR ADVANCED STUDENTS

by

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G. B. KOLHATKAR, M.A., A.I.I.Sc.
and
K. R. JOG, B.Sc.,

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PREFACE

As sciences advance, the lines of demarcation between them tend to disappear and every science, especially in its advanced stage, makes a free use of facts of sister sciences. This is particularly true of Physical Chemistry. To represent different chemical facts by formulæ, to fix up conditions best suited for particular reactions, to study the crystalline condition, to understand a molecular structure, and to investigate such other problems, the help of Mathematics and Physics is indispensable. Hence in working out Problems in Physical Chemistry, the student has to be conversant with these sciences.

We have, therefore, given at the beginning of each chapter a concise mathematical treatment of the subject and derived the necessary formulæ to enable the student to become thoroughly familiar with the theoretical back-ground of the methods used for solving such problems. A few typical problems have been fully worked out and a few more still are given for solution.

Apart from the immediate aim of getting through examinations, the student should bear in mind that physico-chemical methods have a wide application both in theoretical and applied research, and a thorough acquaintance with them will be of material help to him, when in later life, he might be required to face new problems both theoretical and industrial.

We have to thank Mr. V. L. Pradhan for his all-round and ever-ready help which he gave us so willingly and also Mr. V. S. Kulkarni for going through the proof-sheets. Our printer and publisher also deserve our thanks for the pains taken by them for the printing and publication of this book which is of a technical nature.

POONA
15th Aug. 1950

Authors

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ERRATA

PROBLEMS IN PHYSICAL CHEMISTRY by Lele, Kolhatkar and Jog, published by Dastane Bros' Home Service, Ltd., Poona 2.

PAGE	LINE	INCORRECT	CORRECT
11	28	const nt	constant
13	6	1·745	1·785
14	22	Van	van
17	20	28 070	28·070
		25 889	25·889
19	18	$C_6H_5N = \underset{C_6H_5}{\overset{N \rightarrow O}{\vert}}$	$C_6H_5N = \underset{\underset{C_6H_5}{\vert}}{N} \rightarrow O$
31	10	$\frac{3}{2} RT_2$	RT_2
31	10	$\frac{3}{2} RT_1$	RT_1
44	16	− 330520	+ 330520
67	19	*i.e.* L	*Read this "i.e.* L" *at the beginning of the next line (line No. 20)*
70	20	dissociates	dissolves
70	29	$\frac{0·495}{1\ 86}$	$\frac{0·495}{1·86}$
72	10	100·4°C.	100·5°C.
73	7	0·552%	0·552.
80	10	0·942	0·942°
89	1	− 2·303 log	− 2·303 RT log
90	14	$= \frac{Q}{R}$	$= \frac{-Q}{R}$
90	16	$= \frac{Q}{2·303\ R}$	$= \frac{-Q}{2·303\ R}$
96	27	$= \frac{E}{R}$	$= \frac{-E}{R}$

[*Please Turn Over*

97	14, 15, 24, 25	Ω	σ
97	20, 22 23, 24, 25	$e\left(\frac{-E}{RT}\right)$	$e^{\left(\frac{-E}{RT}\right)}$
98	3	$e\left(\frac{-E}{RT}\right)$	$e^{\left(\frac{-E}{RT}\right)}$
104	10	$763 \times$	$760 \times$
104	22	$10^{11\cdot40}$	$10^{11\cdot4}$
106	1	$10^{-2\ 67}$	$10^{-2\cdot67}$
106	10	$+ \frac{1}{2} O$	$+ \frac{1}{2} O_2$
110	30	ethly	ethyl
115	9	50°C.	50.
115	28	326·0 cals.,	326·0 Cals.,
115	28	62·9 cals ,	62·9 Cals ,
115	29	391·7 cals.	391·7 Cals.
116	7	2·8 cals.,	2·8 Cals.,
121	25	$\propto$	∞
123	4, 5	the electricity that flows through the electrolyte.	the total current carried by that ion during electrolysis.
128	20	ion	univalent ion
131	6, 7	*Delete lines 6 and 7 altogether.*	
131	11, 12 13, 14	RT log e	$\frac{RT}{F}$ log e
140	20	=0 7375	=0·7375
159	18	93·168	93·168 r. o.
173	17	$\times$ 2OH')^2	$\times$ (2OH')^2
175	2	*Substitute this line by the following* :—	x_1 and x_2 = the distances from the axis of rotation.
183	6	0·007308	0·007368
187	17	14·092	14·0192
191	11	from 1°F to	through 1°F at

Problems in Physical Chemistry
for Advanced Students

CHAPTER I

GASES AND LIQUIDS

1. **Boyle's Law.**— Let a unit cube (1 c.c.) of a gas at a given temperature and given pressure contain x molecules. As the temperature is fixed, they may be supposed to move with a fixed velocity u. Let the mass of each molecule be m. The change of momentum when a molecule strikes a wall and rebounds is therefore $2\ mu$. As the velocity is u and the distance between the walls is one cm., the total change of momentum per second for each molecule is $(2\ mu \times u) = 2\ mu^2$. For all the x molecules, it will be $2\ xmu^2$. The total force is exerted on the six walls of the cube, and is felt as pressure. The pressure p *i. e.* force on one square cm. (unit surface) is, therefore,

$$\frac{2\ xmu^2}{6} \quad \text{or} \quad p = \frac{1}{3}\ xmu^2.$$

xm (the total mass of the gas per unit volume) is the density ρ of the gas.

Therefore, $$p = \frac{1}{3}\ \rho u^2.$$

ρ can also be written as $\frac{M}{v}$ where, M = mass, and v = volume.

$$p = \frac{1}{3}\frac{M}{v}\ u^2.$$

or, $$pv = \frac{1}{3}\ Mu^2 = \frac{2}{3} \times \frac{1}{2}\ Mu^2.$$

As the temperature is constant, the total kinetic energy $\frac{1}{2}\ Mu^2$ is also constant.

Therefore, pv = constant (Boyle's law).

Combining this with Charles' or Gay Lussac's law,

$$\frac{pv}{T} = \text{constant} \quad (T = \text{temperature in absolute units}).$$

If V is the volume of a gram-molecule at pressure P in atmospheres and at temperature T (absolute), the constant has a definite value and is denoted by R. The equation then assumes the form:

$$\frac{PV}{T} = R;$$

$$\text{or} \quad PV = RT.$$

Generally when n is the number of gram-molecules in volume v at a pressure p and temperature T,

$$pv = nRT.$$

R will have different values according to the unit chosen.

(1) Value of R in litre atmospheres:—

$$R = \frac{PV}{T}$$

$$= \frac{1 \times 22{\cdot}412}{273{\cdot}20}$$

$$= 0{\cdot}08204 \text{ litre atmosphere.}$$

(2) Value of R in ergs:—

$$1 \text{ atmosphere} = 76 \times 13{\cdot}6 \times 981 \text{ ergs.}$$

$$\therefore \quad R = \frac{76 \times 13{\cdot}6 \times 981}{273{\cdot}20} \times \frac{22{\cdot}412}{}$$

$$= 8{\cdot}313 \times 10^7 \text{ ergs.}$$

(3) Value of R in calories:—

$$1 \text{ calorie} = 4{\cdot}186 \times 10^7 \text{ ergs.}$$

$$\therefore \quad R = \frac{8{\cdot}313 \times 10^7}{4{\cdot}186 \times 10^7}$$

$$= 1{\cdot}985 \text{ calories.}$$

2. **Avogadro's Hypothesis.**—Let two gases occupy a volume v at the same temperature and pressure. And let x_1, m_1, u_1 and x_2, m_2, u_2 be their number, mass, and velocity respectively in that volume.

$$\text{For one gas, } pv = \frac{1}{3} x_1 m_1 u_1^2;$$

$$\text{for the other gas, } pv = \frac{1}{3} x_2 m_2 u_2^2.$$

Since the pressure and the volume of the two gases is the same,

$$x_1 m_1 u_1^2 = x_2 m_2 u_2^2.$$

At the same temperature the mean kinetic energy of each gas is the same, *i. e.*

$$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2,$$

$$\therefore \quad x_1 = x_2.$$

The number of molecules of two gases at the same temperature and pressure in the same volume is the same (**Avogadro's Hypothesis**).

3. **Graham's Law.**—

$$p = \frac{1}{3} \rho u^2, \quad \text{where } \rho = xm = \text{density of the gas.}$$

$$\therefore \quad \frac{3p}{\rho} = u^2;$$

$$\text{or,} \quad u = \sqrt{\frac{3p}{\rho}}.$$

The velocity of a gas at the same pressure is inversely proportional to the square root of its density. A light gas, therefore, diffuses faster than a heavy one (**Graham's Law**).

4. **Molecular Velocity.**— Molecular velocity of a gas can be calculated from the equation, $u = \sqrt{\frac{3p}{\rho}}$.

5. **The Specific Heats.**—The kinetic energy $\left(\frac{1}{2} x\, mu^2\right)$ of a perfect gas, being all translational, is proportional to its absolute temperature T_1. The kinetic energy of G. M. V. of the gas at T_1 is $\frac{1}{2} x\, mu_1^2$ where u_1 is the velocity of the gas at the temperature T_1 and x is the number of molecules in a gram molecule.

But $\frac{1}{3} x\, mu_1^2 = PV$.

Since $PV = RT$ for a gram molecule,

$$\frac{1}{3} x\, mu_1^2 = RT_1$$

or $$\frac{1}{2} x\, mu_1^2 = \frac{3}{2} RT_1 \quad \ldots \quad \ldots \quad (A).$$

Similarly at a tempeiature T_2,

$\frac{1}{2} x\, mu_2^2 = \frac{3}{2} RT_2$, where u_2 is the velocity at T_2 (B).

The difference in the kinetic energy of the gas at the two temperatures is $= \frac{1}{2} x\, mu_2^2 - \frac{1}{2} x\, mu_1^2$,

$$= \frac{3}{2} R(T_2 - T_1).$$

If $T_2 - T_1$ is one, the difference in the kinetic energy of the gas (due to the heat absorbed by the gas at constant volume to raise its temperature through one degree) is the specific heat (C_v) of the gas at constant volume.

Therefore, $C_v = \frac{3}{2} R$.

But, $R = 1{\cdot}985$ calories.

$$\therefore \quad C_v = \frac{3 \times 1{\cdot}985}{2},$$

$$= 2{\cdot}9775 \approx 3 \text{ calories}.$$

If the pressure is kept constant during the rise of temperature from T_1 to T_2, the volume will be changed from V_1 to V_2,

$$PV_1 = RT_1,$$

$$PV_2 = RT_2,$$

$$P(V_2 - V_1) = R(T_2 - T_1).$$

If the temperature difference $(T_2 - T_1)$ is one,

$$P(V_2 - V_1) = R$$

$$= 2 \text{ calories approximately}.$$

$P(V_2 - V_1)$ is the work done during expansion. The heat absorbed by a gas to raise its temperature through one degree at constant pressure, is C_p. The difference of the specific heat at constant pressure (C_p) and the specific heat at constant volume (C_v) is, therefore, equal to 2.

$$C_p - C_v = 2$$

$$i.e. \quad C_p - 3 = 2.$$

Therefore, $$C_p = 5.$$

The ratio $\frac{C_p}{C_v}$ (usually called y) is $\frac{5}{3} = 1{\cdot}666$, for a perfect gas *i.e.*, one in which no internal work is done in raising the temperature. $\frac{C_p}{C_v}$, for monoatomic gases, approximates this value;

e. g., for Helium, it is 1·666,
and for Argon, it is 1·67.

For a perfect gas all the heat absorbed at constant volume increases its kinetic energy.

For diatomic gases $\frac{C_p}{C_v} \approx 1{\cdot}4$. For gases containing more than two atoms $\frac{C_p}{C_v}$ is still less, and approaches unity, as the number of atoms in the molecule increases. Since the internal work increases with the number of atoms in a molecule, the equation $\frac{C_p}{C_v} = \frac{5}{3}$, true for a monoatomic gas, must be modified by adding x (*i. e.*, the heat required for internal work) both to the numerator and denominator of the right hand side. For gases containing two or more atoms in a molecule the equation becomes

$$\frac{C_p}{C_v} = \frac{5 + x}{3 + x}.$$

6. **The Mean Free Path,** *i. e.*, the distance a molecule of a gas can travel before colliding with another molecule, depends on its velocity, density and viscosity; and these magnitudes can be shown to be related by the following equation :

$$\eta = \frac{1}{3}\rho\lambda u$$

where, η = viscosity,
ρ = density,
λ = mean free path, and
u = velocity.

But $$u = \sqrt{\frac{3p}{\rho}}\,.$$

$\therefore$ $$\eta = \lambda\sqrt{\frac{p\rho}{3}}$$

or $$\lambda = \eta\sqrt{\frac{3}{p\rho}}\,.$$

$\left(\text{The frequency of collision is given by } \frac{u}{\lambda}\right)$.

7. **Van der Waals' Equation and Critical Constants.**—For an ideal gas the value of pv should be independent of pressure. It is, however found that this is not true. At ordinary temperature, in the case of most gases, pv first diminishes and then increases with rise of pressure, while for helium and hydrogen pv at ordinary temperature increases with pressure. Van der Waals modified the general gas equation by introducing two constants, 'a' to represent the attraction between the molecules, and 'b' to represent their actual volume. This equation is, therefore, written as follows :—

$$\left(P + a \cdot \frac{1}{V^2}\right)\left(V - b\right) = RT.$$

The above equation assumes that one gram molecule is present in V litres. The general equation when 'n' molecules are present in v litres is

$$\left(p + \frac{an^2}{v^2}\right)\left(v - nb\right) = nRT$$

since total attraction is directly proportional to the square of the number of gram molecules, and inversely proportional to the square of the volume.

On simplification, one gets the following cubic equation in V,

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0.$$

At a particular temperature and pressure (called the critical temperature and pressure), the three roots of the equation become identical, *i.e.*, V has only one value. Let it be v_c at the pressure p_c, and the temperature T_c,

$$\text{Then,} \qquad (V - v_c)^3 = 0.$$

$$\therefore \quad V^3 - 3v_c V^2 + 3v_c^2 V - v_c^3 = 0.$$

Van der Waals' equation for critical temperature and pressure will be

$$V^3 - \left(b + \frac{RT_c}{p_c}\right)V^2 + \frac{a}{p_c}V - \frac{ab}{p_c} = 0.$$

Equating the coefficients of the like powers of v,

$$3v_c = b + \frac{RT_c}{p_c},$$

$$3v_c^2 = \frac{a}{p_c}, \text{ and}$$

$$v_c^3 = \frac{ab}{p_c},$$

$$\text{one gets,} \quad v_c = 3b,$$

$$p_c = \frac{a}{27b^2},$$

$$T_c = \frac{8}{27} \cdot \frac{a}{Rb}.$$

$$\frac{RT_c}{p_c v_c} = \frac{8}{3} = 2{\cdot}67.$$

N. B.—It should be noted that the value of v_c at T_c and p_c is 2·67 times less than that found by the general equation $pv = n\text{RT}$.

8. **The Limiting Density.**—If W is the mass of a gas at a pressure 'p', and volume 'v', the quotient $\frac{W}{pv}$ will be its density per unit pressure. According to Boyle's Law, pv is constant for a given temperature; then $\frac{W}{pv}$ should be constant at a given temperature for an ideal gas, *i. e.*, a gas whose particles do not exert any attraction, or do not occupy appreciable space. In the case of all gases, this, however, is not the case. On account of the slight attraction (a) between the molecules and

the actual volume (b) that the molecules of (a non ideal or) an imperfect gas occupy, the relation will only be true, when the pressure approaches zero and the volume approaches infinity.

At the limiting value p_0v_0 (for a pressure (p_0) approaching zero), $\frac{W}{p_0v_0}$ (the limiting density) will be constant at a given temperature for any gas. The normal density $\frac{W}{p_1v_1}$ is commonly measured at p_1, when the pressure (p_1) is one atmosphere.

$$\frac{W}{p_1v_1} = \text{normal density.} \qquad \text{Multiply by } \frac{p_1v_1}{p_0v_0}$$

$$\frac{W}{p_1v_1} \times \frac{p_1v_1}{p_0v_0} = \text{normal density} \times \frac{p_1v_1}{p_0v_0} = \frac{W}{p_0v_0}.$$

But, $\frac{W}{p_0v_0}$ is limiting density.

$$\therefore \text{ limiting density } = \text{normal density} \times \frac{p_1v_1}{p_0v_0}.$$

For gases deviating only slightly from Boyle's Law, the relative variation of pv is proportional to p, *i. e.*,

$$\frac{p_0v_0 - pv}{pv} = a\,p\,;$$

a is known as the compressibility coefficient.

If p_1 is the pressure of one atmosphere, and v_1 the corresponding volume, then

$$\frac{p_0v_0 - p_1v_1}{p_1v_1} = a,$$

$$i.\,e. \quad \frac{p_0v_0}{p_1v_1} - 1 = a.$$

$$\therefore \quad \frac{p_0v_0}{p_1v_1} = (1 + a).$$

$$\therefore \quad \frac{p_1v_1}{p_0v_0} = \frac{1}{1 + a}.$$

Substituting this value in the above equation, we get,

$$\text{Limiting density} = \frac{\text{Normal density}}{1 + a}.$$

The value of a can be determined from two readings of pv between zero and one atmosphere.

9. **Surface Tension.**—(*i*) Molecular Weight (*ii*) Degree of Association (Ramsay and Shields equation).

γ, the surface tension, can be calculated from the rise of a liquid in a capillary tube, with the help of the following equation :—

$$\gamma = \frac{1}{2} grhd$$

where, g = gravity (981·1 cm. / sec.^{2})
r = radius in cm.
h = height in cm.
d = density gm/c. c.

If γ_1 and γ_2 are the surface tensions of the two liquids, and m_1 and m_2 are the masses of single drops of the two liquids which remain suspended from a tube, then,

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}.$$

$$\gamma (Mv)^{\frac{2}{3}} = \text{molecular surface energy, (volume) } v = \frac{1}{d}.$$

The relation of molecular surface energy with temperature is given by the following equation (Ramsay and Shields),

$$\frac{\gamma_1 (Mv_1)^{\frac{2}{3}} - \gamma_2 (Mv_2)^{\frac{2}{3}}}{t_2 - t_1} = 2{\cdot}121.$$

The temperature coefficient of surface energy is constant. This is the case of liquids which are not associated. If the molecules in the liquid are associated to the extent x, the above equation becomes,

$$\frac{\gamma_1 (x\, Mv_1)^{\frac{2}{3}} - \gamma_2 (x\, Mv_2)^{\frac{2}{3}}}{t_2 - t_1} = 2{\cdot}121.$$

10. **Viscosity.**—It is measured by noting the time required for a definite volume of a liquid to run th rough a definite length in a tube under definite pressure. The coefficient of viscosity (η) is expressed by the equation :—

$$\eta = \frac{\pi p t r^4}{8 lv}$$

where, p = pressure,
t = time in seconds,
r = radius,
l = length, and
v = volume.

Dunstan discovered the following relationship between viscosity and molecular volume :—

$$\frac{d}{m} \cdot \eta \times 10^6 = 40 \text{ to } 60$$

This holds only for normal liquids. Associated ones give greater values.

11. **Parachor.**—It is an additive property modified by constitutive influences and is given by the following formula :—

$$P = \left(\frac{M}{D - d}\right) \gamma^{\frac{1}{4}}$$

where, M = molecular weight,
D = the density of the liquid,
d = density of the vapour of the liquid, and
γ = surface tension.

As d is very small compared with D, it is neglected in approximate work.

Problems with Solutions

Problem 1. A porcelain bulb containing initially 285 c.c. of air at $T_1 = 290°$ and $p = 766{\cdot}4$ m.m. was heated in the vapour of boiling cadmium. The bulb was then sealed. The volume of the contents measured afterwards at the initial temperature and pressure was 72 c. c. What was the temperature of the boiling cadmium ?

Solution : The volume of 285 c. c. (v_2) at the temperature of boiling cadmium (T_2) is reduced to 72 c. c. (v_1), when cooled to T_1, 290°. The pressure remained the same at both the temperatures. If T_2 be the temperature of boiling cadmium,

$$\frac{v_1}{T_1} = \frac{v_2}{T_2}.$$

$$\therefore \quad T_2 = \frac{v_2 T_1}{v_1},$$

$$= \frac{285 \times 290}{72},$$

$$= 1148.$$

Ans. The temperature of boiling cadmium, (T_2) = 1148°

Problem 2. Ethyl ether ($C_4H_{10}O$) is to be vapourised in a Victor Meyer apparatus at 100° C. and 760 mm., and the air collected at 15° over mercury, the maximum capacity of the collecting tube (t = 12°) being 100 c. c. The absolute density of H_2 at N. T. P. is 0·00009. What is the greatest weight of ether that can be used.

Note :—The volume of the collecting tube will practically remain constant (100 c. c.), when the temperature is altered from 12°C. to 15°C. since the coefficient of expansion of glass is very small, as compared to that of the gas.

***Solution* :** Converting this volume, which corresponds to the volume of ethyl ether at 15°, to that at N. T. P.,

$$\frac{273 \times 100}{288} = 94{\cdot}8.$$

The weight of this volume of ether is the greatest weight that can be used The density of ether vapour can be calculated from that of H_2,

$$\frac{0{\cdot}00009 \times 74}{2} = 0{\cdot}00333.$$

The weight of 94·8 c. c. of ether at N. T. P. is

$$94{\cdot}8 \times 0{\cdot}00333 = 0{\cdot}3157.$$

Ans. The greatest weight of ether that can be used is 0·3157 gram.

Problem 3. 0·02 g. of $NaHCO_3$ when introduced into a constant volume apparatus kept at 300°C. gives rise by its complete decomposition to a pressure increase of 98 mm. of Hg. Calculate the volume of the apparatus.

Solution: The decomposition of $NaHCO_3$ is represented by the equation, $2\ NaHCO_3 = Na_2CO_3 + H_2O + CO_2$.
168 2 mols.

168 grams of $NaHCO_3$ give two mols. (one of H_2O and one of CO_2). Hence 0·02 gm. will give

$$\frac{0{\cdot}02 \times 2}{168} \text{ mols. or } \frac{0{\cdot}02 \times 2 \times 22{\cdot}4}{168} \text{ litres at N. T. P.}$$

The volume of the apparatus can be calculated by making use of the equation

$$\frac{VP}{T} = \frac{V_1P_1}{T_1}$$

$$\frac{0{\cdot}02 \times 2 \times 22{\cdot}4 \times 760 \times 573}{168 \times 273 \times 98} = 0{\cdot}08681 \text{ litre.}$$

$$= 86{\cdot}81 \text{ c. c.}$$

Ans. The volume of the apparatus is 86·81 c. c.

Problem 4. Two vessels *A* and *B* containing respectively chlorine and a mixture of oxygen and another gas, are connected by means of a short capillary tube. The mixture contains 10 p.c. of oxygen. After diffusion for a limited time, the chlorine in *A* is absorbed by potash, and the remaining gas contains 11·05 p. c. of oxygen. What is the density of the second gas?

Note :—Gases in a dilute mixture diffuse independently of each other. The presence of 'Cl' has no influence on the diffusion of the other gases.

Solution : The diffusion is proportional to $\sqrt{\frac{1}{d}}$, where d is the density of the gas.

Let x be the amount of the mixture of oxygen and the other gas. The amount of oxygen diffused,

$$= 0{\cdot}10x\sqrt{\frac{1}{d}}.$$

The amount of the other gas diffused,

$$= 0{\cdot}90x\sqrt{\frac{1}{d_1}}.$$

d and d_1 being the densities of oxygen and of the other gas respectively.

$$\frac{0{\cdot}10x\sqrt{\dfrac{1}{d}}}{0{\cdot}90x\sqrt{\dfrac{1}{d_1}}} = \frac{11{\cdot}05}{88{\cdot}95}$$

$$\frac{d_1}{d} = \left(\frac{11{\cdot}05}{88{\cdot}95} \times \frac{90}{10}\right)^2$$

$$d \text{ of oxygen} = \frac{32}{22{,}400}$$

$$d_1 \text{ of other gas} = \left(\frac{11{\cdot}05 \times 90}{88{\cdot}95 \times 10}\right)^2 \times \frac{32}{22{,}400}$$

$$= 1{\cdot}785 \times 10^{-3} \text{ gram per c. c.}$$

Ans. $1{\cdot}745 \times 10^{-3}$ gram per c. c.

Problem 5. The density of hydrogen at 0° and 760 mm. pressure is 0·00009 gram per c.c. Find the root mean square velocity of hydrogen molecules.

Solution : The root mean square velocity is given by the equation, $u = \sqrt{\dfrac{3p}{\rho}}$.

Substituting the values of p (dynes) and ρ,

$$u = \sqrt{\frac{3 \times 76 \times 13{\cdot}59 \times 981}{0{\cdot}00009}}$$

$$= 183800 \text{ cms. per sec.}$$

Ans. 1838 m. per sec.

Problem 6. For chlorine, $a = 5{\cdot}34 \times 10^6$ atm. per $(\text{c.c.})^2$ and $b = 46$ c. c./mol. Calculate the pressure of Cl_2 at 50°C. when 2 mols. of the gas occupy 30 *l*.

Solution : Using the equation,

$$\left(p + \frac{n^2a}{v^2}\right)(v - nb) = n\text{RT}.$$

In this equation, the value of v expressed in c. c.s, is 30,000 and the value of R in centimeter-atmospheres, is 82·04.

$$\left(p + \frac{4 \times 5{\cdot}34 \times 10^6}{(30{,}000)^2}\right)(30{,}000 - 92) = 2 \times 82{\cdot}04 \times 323$$

$$(p + 0{\cdot}02373)\, 29{,}908 = 53{,}037$$

$$p + 0{\cdot}02373 = \frac{53{,}030}{29{,}908}$$
$$= 1{\cdot}774.$$
$$\therefore \quad p = 1{\cdot}774 - 0{\cdot}02373$$
$$= 1{\cdot}7502$$

Ans. The pressure of chlorine is 1·7502 atmospheres.

Problem 7. For H_2, $T_c = 33{\cdot}18^\circ$ abs. and $p_c = 12{\cdot}80$ atmospheres. Calculate a and b, and find at what temperature 8 gms. of H_2 will occupy 100 l under a pressure of 1 atm.

Solution : Calculate b first,

$$p_c = \frac{a}{27b^2}$$
$$T_c = \frac{8a}{27Rb}$$
$$\frac{T_c}{p_c} = \frac{8a}{27Rb} \times \frac{27b^2}{a}$$
$$\frac{33{\cdot}18}{12{\cdot}8} = \frac{8b}{R}$$

The value of R (l-atm-mol.) = 0·08204.

$$\therefore \quad b = \frac{33{\cdot}18 \times 0{\cdot}08204}{8 \times 12{\cdot}8}$$
$$= 0{\cdot}02660.$$

To calculate a,

$$p_c = \frac{a}{27b^2}$$
$$a = p_c \times 27b^2$$
$$= 12{\cdot}80 \times 27 \times (0{\cdot}02660)^2$$
$$= 0{\cdot}2444.$$

Substituting the respective values of a and b in Van der Waals' equation,

$$\left\{p + a\left(\frac{n}{v}\right)^2\right\}(v - nb) = nRT$$
$$\left(1 + \frac{(4)^2 \times 0{\cdot}2444}{(100)^2}\right)(100 - 4 \times 0{\cdot}02660)$$
$$= 4 \times 0{\cdot}08204 \times T.$$

As v is expressed in l, R is taken as 0·08204.

$$(1 + 3 \cdot 9104 \times 10^{-4})(100 - 0 \cdot 1064) = 0 \cdot 32836 T$$

$$T = \frac{1 \cdot 00039104 \times 99 \cdot 8936}{0 \cdot 32836} = 304 \cdot 2.$$

Ans. (1) $a = 0 \cdot 2444$; $b = 0 \cdot 02660$.

(2) 304·2 Absolute, or, 31·2°C.

Problem 8. If a, b, and R for carbon dioxide have respectively the values of 0·00874; 0·0023 and $\frac{1 \cdot 00646}{273}$, find the critical temperature of carbon dioxide.

Solution:

$$T_c = \frac{8a}{27Rb}$$

$$= \frac{8 \times 0 \cdot 00874 \times 273}{27 \times 1 \cdot 00646 \times 0 \cdot 0023}$$

Ans. 305·4 Absolute or 32·4°C.

Problem 9. Moles and Salazer (Anales Soc. Espan. Fis. Quin. 1932, 30, 182) found the density of carbon monoxide under a pressure of 1 atmosphere and at 0°C, to be 1·25010 gms. per litre. The value for $(1 + \lambda)$ was 1·0050. The gram molecule occupies a volume of 22·414 litres. Calculate the molecular weight of carbon monoxide, and the atomic weight of carbon.

$$\text{The limiting density} = \frac{\text{The normal density}}{1 + \lambda}$$

$$= \frac{1 \cdot 25010}{1 \cdot 0050}$$

$$= 1 \cdot 244.$$

$$\left.\begin{array}{r}\text{The molecular weight} \\ \text{of carbon monoxide}\end{array}\right\} = 1 \cdot 244 \times 22 \cdot 414$$

$$= 27 \cdot 88.$$

The atomic weight of Carbon = 27·88 − 16 = 11·88.

Ans. (1) Molecular Wt. of carbon monoxide, 27·88;

(2) Atomic Wt. of carbon, 11·88.

Problem 10. The following values of pv and p_0v_0 were found for oxygen.

p_0v_0	pv
139, 769	139, 628
139, 087	138, 959
56, 311	56, 256

Calculate the mean value of a and the ideal weight of a litre at N. T. P., if that actually found is 1·429 gms.

Solution :

$$\frac{pv}{p_0v_0} = \frac{1}{1 + a}$$

$$(1) \quad \frac{139,628}{139,769} = 0{\cdot}9991 \qquad : a = 0{\cdot}0009$$

$$(2) \quad \frac{138,959}{139,087} = 0{\cdot}9992 \qquad : a = 0{\cdot}0008$$

$$(3) \quad \frac{56,256}{56,311} = 0{\cdot}9988 \qquad : a = 0{\cdot}0012$$

The mean value of a = 0·00097

The ideal weight of a litre of oxygen

$$= \frac{1{\cdot}429}{1{\cdot}00097}$$

Ans. 1·428 gm.

Problem 11. 50 c. c. of water in a stalagmometer give 145 drops. The surface tension of water is 72 dynes per cm., whilst that of ether is 17 dynes per cm. Calculate the weight of one drop of ether under the same conditions with the same stalagmometer.

Solution : The relation between the weight of one drop and the surface tension is given by the equation,

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \quad \left(m_1 \text{ and } m_2 \text{ are the weights of drops of the respective liquids.} \right)$$

Substituting the values for water and ether,

$$\frac{72}{17} = \frac{50}{145} \div m_2$$

$$\therefore \quad m_2 = \frac{50}{145} \times \frac{17}{72} = 0{\cdot}08142.$$

Ans. 0·08142 gm. (the weight of one drop of ether).

Problem 12. Normal butyl alcohol at the temperature $t°$ and density d rose to a height h in a capillary tube of radius 0·01425 cm. Calculate its factor of association and molecular weight from the following data :

t°C	d	h
17·4	0·8115	4·305
45·7	0·7907	4·005

Solution : First find the surface tension at the different temperatures : $\gamma_1 = \frac{1}{2}$ grhd

$$= 0{\cdot}5 \times 981{\cdot}1 \times 0{\cdot}01425 \times 4{\cdot}305 \times 0{\cdot}8115$$
$$= 24{\cdot}420$$
$$\gamma_2 = 0{\cdot}5 \times 981{\cdot}1 \times 0{\cdot}01425 \times 4{\cdot}005 \times 0{\cdot}7907$$
$$= 22{\cdot}136$$

The mean molecular weight between 17·4°C. and 45·7°C. is given by the equation,

$$\frac{\gamma_1 (m / d_1)^{\frac{2}{3}} - \gamma_2 (m / d_2)^{\frac{2}{3}}}{t_2 - t_1} = 2{\cdot}121 ;$$

i. e.
$$\frac{m^{\frac{2}{3}} \left[\gamma_1 \left(\frac{1}{d_1} \right)^{\frac{2}{3}} - \gamma_2 \left(\frac{1}{d_2} \right)^{\frac{2}{3}} \right]}{t_2 - t_1} = 2{\cdot}121.$$

Substituting the values, we get,

$$\frac{m^{\frac{2}{3}} \left[24{\cdot}420 \left(\frac{1}{0{\cdot}8115} \right)^{\frac{2}{3}} - 22{\cdot}136 \left(\frac{1}{0{\cdot}7907} \right)^{\frac{2}{3}} \right]}{45{\cdot}7 - 17{\cdot}4} = 2{\cdot}121 ;$$

i. e.
$$\frac{m^{\frac{2}{3}} [28{\cdot}070 - 25{\cdot}889]}{28{\cdot}3} = 2{\cdot}121.$$

$$\therefore \quad m^{\frac{2}{3}} = \frac{2{\cdot}121 \times 28{\cdot}3}{2{\cdot}181}$$

$$\therefore \quad m = \left(\frac{2{\cdot}121 \times 28{\cdot}3}{2{\cdot}181} \right)^{\frac{3}{2}}$$
$$= 144{\cdot}38.$$

The factor of association can be found by dividing the mean molecular weight by the theoretical molecular weight (74) of butyl alcohol (C_4H_9OH)

$$\frac{144{\cdot}38}{74} = 1{\cdot}949$$

Ans. (1) 1·949 is the factor of association.

(2) 144·38, molecular weight of butyl alcohol (mean value.)

Problem 13. The viscosity of nitromethane (CH_3NO_2) is 0·00627 at 25°C. Its density is 1·1312. What conclusions do you draw as to its molecular complexity in the liquid state ?

Solution : The molecular weight of CH_3NO_2 is 61. Using Dunstan's equation,

$$\frac{d}{m} \cdot \eta \times 10^6 = 40 \text{ to } 60,$$

$$\text{constant} = \frac{1{\cdot}1312}{61} \times 0{\cdot}00627 \times 10^6.$$

$$= 116{\cdot}27$$

Ans. The value of the constant is considerably greater than 60. The liquid is, therefore, associated.

Problem 14. From the following density and surface tension data, calculate the parachors of the two substances and compare them with the calculated values.

Substance	Temperature	Density	Surface Tension
Phosphorus tribromide	24	2·883	45·8
,,	33	2·861	44·1
Azoxybenzene	51	1·145	43·34
,,	77·5	1·122	40·26

Solution : The densities in the vapour condition of both the substances may be neglected. *m* of phosphorus tribromide is 271.

At the temperature 24,

$$p = \left(\frac{m}{d}\right) \gamma^{\frac{1}{4}}$$

$$= \left(\frac{271}{2{\cdot}883}\right) 45{\cdot}8^{\frac{1}{4}}$$

$$= 244{\cdot}54.$$

At the temperature 33,

$$p = \left(\frac{271}{2{\cdot}861}\right) 44{\cdot}1^{\frac{1}{4}}$$

$$= 244{\cdot}1. \qquad (244{\cdot}32 \text{ mean value}).$$

Theoretical value of parachor for PBr_3 is,

$$\{[1\,P = 37{\cdot}7] + [3\,Br = (68 \times 3)]\} = 241{\cdot}7.$$

m of Azoxybenzene is 198.

At the temperature 51,

$$p = \left(\frac{198}{1{\cdot}145}\right) 43{\cdot}34^{\frac{1}{4}}$$

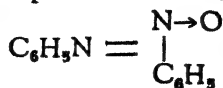
$$= 443{\cdot}7.$$

At the temperature 77·5,

$$p = \left(\frac{198}{1{\cdot}122}\right) 40{\cdot}26^{\frac{1}{4}}$$

$$= 443{\cdot}53 \qquad (443{\cdot}61 \text{ mean value}).$$

Theoretical value of parachor for azoxybenzene,

$$C_6H_5N = \underset{\displaystyle C_6H_5}{\overset{\displaystyle N \rightarrow O}{|}}$$

12 C = 57·6, (12 × 4·8); 10 H = 171·0, (10 × 17·1);
2 N = 25, (2 × 12·5); 1 O = 20·0;
7 double bonds = 162·4, (7 × 23·2);
2 six membered rings = 12·2, (2 × 6·1). Total = 448·2
1 co-ordinate link ... ... = − 1·6
Adding up all these values = (448·2 − 1·6)
= 446·6.

Ans. Phosphorus tribromide (1) 244·32 Calculated.
(2) 241·70 Theoretical.

Azoxybenzene (1) 443·61 Calculated
(2) 446·60 Theoretical.

Problem 15. Liquids C_6H_5Cl and H_2O are practically immiscible. At 90° and 91° their vapour pressures are as follows :—

Liquids	Temperature	Pressure
C_6H_5Cl	90°	208·35
,,	91°	215·80
H_2O	90°	525·45
,,	91°	545·80

At intermediate temperature the variation of pressure may be assumed to be linear. What is the boiling point of the mixture under an external pressure of 740·2 mm., and what will be the percentage composition of the distillate.

Solution : Total pressures at 90° and 91° are :

at 90°,	H_2O	525·45,
	C_6H_5Cl	208·35
	total	733·80 ;
and at 91°,	H_2O	545·80
	C_6H_5Cl	215·80
	total	761·60

The increase in pressure from 90° to 91° is,

$$761{\cdot}60 - 733{\cdot}80 = 27{\cdot}80.$$

At the external pressure of 740·2 mm., the increase is $740{\cdot}2 - 733{\cdot}8 = 6{\cdot}4$ mm.

The increase in the boiling point will be, $\frac{6{\cdot}4}{27{\cdot}8} = 0{\cdot}2302.$

$\therefore$ The boiling point $= 90 + 0{\cdot}2302$

$= 90{\cdot}2302.$

To find the percentage of water and chlorobenzene in the distillate, calculate the respective increase in pressure from 90° to 91° for water and chlorobenzene. $H_2O = (545{\cdot}80 - 525{\cdot}45) = 20{\cdot}35$, and $C_6H_5Cl = 215{\cdot}80 - 208{\cdot}35 = 7{\cdot}45$.

Therefore, in the total increase of 27·8 in the vapour pressure, the increase in pressure for water vapour is 20·35, and that for

chlorobenzene is 7·45. For the total increase of 6·4, the increase in respective pressures will be,

$$\text{for water} = \frac{6{\cdot}4 \times 20{\cdot}35}{27{\cdot}8} = 4{\cdot}685,$$

$$\text{and for chlorobenzene} = \frac{6{\cdot}4 \times 7{\cdot}45}{27\ 8} = 1{\cdot}715.$$

The individual pressures at 90·2302° will be, H_2O, (525·45 + 4·685) = 530·135, and C_6H_5Cl, (208·35 + 1·715) = 210 065.

The percentage by volume of H_2O and C_6H_5Cl in vapour condition will be,

$$\text{for } H_2O = \frac{530{\cdot}135 \times 100}{740{\cdot}2} = 71{\cdot}63,$$

$$\text{and for } C_6H_5Cl = \frac{210{\cdot}065 \times 100}{740\ 2} = 28{\cdot}37.$$

To find the percentage by weight, multiply the above percentages by volume, by their respective molecular weight.

For water, 71·63 × 18 = 1289·34,
and for chlorobenzene, 28·37 × 112·5 = 3192·00.
The total = 4481·34.

$$\text{The amount of } C_6H_5Cl \text{ will be} = \frac{3192 \times 100}{4481{\cdot}34} = 71{\cdot}22\%.$$

$$\text{The amount of } H_2O \text{ will be} = \frac{1289{\cdot}34 \times 100}{4481{\cdot}34} = 28{\cdot}77\%.$$

Ans. (1) The boiling point of the mixture at the external pressure of 740·2 mm. = 90·23°.

(2) Percentage by weight in the distillate,
H_2O = 28 77 %.
C_6H_5Cl = 71·22 %.

Problem 16. If the volume of an aqueous solution of benzoic acid of known strength be 1 litre, and that of the ether added each time be 200 c c., find the quantity of the acid which will be left in the water at the end of the third extraction. The partition coefficient of benzoic acid between water and ether is 1/80.

Solution: Let x be the amount of benzoic acid in 1000 c. c. of water in the beginning, and y be the amount of benzoic acid extracted in 200 c. c. of ether. Then after

1st extraction :—

$$\frac{x-y}{1000} \div \frac{y}{200} = \frac{1}{80}$$

$$\frac{(x-y)200}{1000 \times y} = \frac{1}{80}$$

$$\frac{x-y}{5y} = \frac{1}{80}$$

$$\frac{x-y}{y} = \frac{1}{16}$$

$$y = 16(x-y)$$

$$= 16x - 16y$$

$$17y = 16x$$

$$y = \frac{16}{17}x.$$

Hence, $x - \frac{16x}{17}$ *i. e.* $\frac{17x - 16x}{17} = \frac{x}{17}$ is the amount of benzoic acid in water at the end of the 1st extraction.

2nd extraction :—

$\frac{x}{17}$ is the amount of benzoic acid in 1000 c. c. of water at the beginning of 2nd extraction and y_2 benzoic acid extracted in 200 c. c. of ether

$$\frac{x - 17y_2}{17 \times 1000} \times \frac{200}{y_2} = \frac{1}{80}$$

$$\frac{x - 17y_2}{17 \times 5 \times y_2} = \frac{1}{80}$$

$$\frac{x - 17y_2}{y_2} = \frac{17}{16}$$

$$16(x - 17y_2) = 17y_2$$

$$\frac{16}{17}x - 16y_2 = y_2$$

$$17y_2 = \frac{16}{17}x$$

$$y_2 = \frac{16x}{17 \times 17}$$

Amount of benzoic acid in water at the end of the 2nd extraction, or at the beginning of the *3rd extraction*,

$$= \frac{x}{17} - \frac{16x}{17 \times 17}$$

$$= \frac{x}{17}\left(1 - \frac{16}{17}\right)$$

$$= \frac{x}{17}\left(\frac{1}{17}\right)$$

i.e. $$= \frac{x}{(17)^2}$$

At the end of the third extraction the amount of benzoic acid in water will therefore, be

$$\frac{x}{(17)^2} \times \frac{1}{17} = \frac{x}{(17)^3}$$

$$= 0{\cdot}0002008x$$

or $$= 0{\cdot}02008 \text{ per cent.}$$

Ans. 0·02008 per cent. of the original amount remains in the aqueous layer at the end of the 3rd extraction.

Problem 17. At 25°C. a solution of iodine in water containing 0·0516 g. per litre is in equilibrium with CCl_4 solution containing 4·412 g. of iodine per litre. The solubility of iodine in water at 35°C. is 0·340 per litre. What is its solubility in CCl_4?

The partition coefficient,

$$K = \frac{C_1}{C_2}$$ where C_1 and C_2

are the concentrations of the iodine in water and in carbon tetrachloride. Substituting the values given above

$$K = \frac{0{\cdot}0516}{4{\cdot}412}$$

and also, $K = \frac{0{\cdot}340}{x}$; where x is the solubility of iodine in grams per litre in carbon tetrachloride at 35°C. Equating the two equations

$$\frac{0{\cdot}0516}{4{\cdot}412} = \frac{0{\cdot}340}{x}$$

$$x = \frac{0{\cdot}340 \times 4{\cdot}412}{0{\cdot}0516}$$

$$= 29{\cdot}07$$

Ans. The solubility of iodine in carbon tetrachloride at 35°C. is 29·07 g/l.

Problems for Solution

Problem 18. Calculate the amount of work required to compress a litre of a gas from a pressure of one atmosphere to two atmospheres at 25°C.

Ans. 16·7 cals.

Problem 19. Calculate the velocity of a molecule of nitrogen at 0°C. given that one atmosphere equals 1·013 $\times 10^6$ dynes per sq. cm. and that the gram molecular volume is 22,400 c. c.

Ans. 4·9307 $\times 10^4$ cms. per sec.

Problem 20. A natural water on boiling gave a mixture of the following composition :

O_2 20·9%; N_2 39·5 %; CO_2 39·6%.

Assuming that the water had dissolved these gases from the air with which it had been previously in contact, calculate the composition of the air.

Solubility coefficients of, O_2 = 0·04; N_2 = 0·02; and CO_2 = 1·79 respectively.

Ans. O_2 = 20·83%; N_2 = 78·74%; CO_2 = 0·43%.

Problem 21. The relative rates of diffusion of oxygen, hydrogen and nitrogen are respectively 0·96, 3·80 and 1·015. What deductions may be drawn from these figures concerning the density of nitrogen ?

Ans. The density of nitrogen as compared to that of hydrogen is 14·06, and to that of oxygen is 14·36.

Problem 22. If 50 c. c. of hydrogen take 10 minutes to diffuse out of a vessel, how long will 20 c. c. of nitrogen take to diffuse under the same conditions.

Ans. 15 minutes.

Problem 23. If 50 volumes of hydrogen take 85 seconds to diffuse from a vessel, how long would it take 35 volumes of nitrous oxide to do so under the same conditions ?

Ans. 279 seconds.

Problem 24. If, in Soret's apparatus 100 c. c. of HCl gas had been mixed with oxygen and 18 c. c. had diffused in half an hour, what molecular weight would you assign to an acid gas 12 c. c. of which (out of 100 c. c.) diffused under the same conditions ?

Ans. 82, molecular weight of the gas.

Problem 25. It was found that ozonised oxygen containing 86·16 p. c. ozone by volume required 450 seconds to diffuse whereas the same volume of oxygen required 367·4 seconds under the same conditions. Find the density of ozone.

Ans. 22·95.

Problem 26. To determine the molecular weight of radon, Perkin found the rate of diffusion of radon and compared it with that of mercury vapour. 0·025 c. c. of radon diffused through a porous membrane in the same time as 0·027 c. c. of mercury vapour. Mercury vapour like radon, is mono-atomic and its atomic weight is 200·6. Calculate the molecular weight of radon.

Ans. 234.

Problem 27. Soret found that when chlorine mixed with oxygen diffused through a small aperture into oxygen, the proportion of the diffused chlorine to that in the remaining vessel in 45 minutes was represented by the number 0·2270; whilst in a similar experiment made with ozonised oxygen the proporrion of the diffused ozone to that remaining in the vessel in 45 minutes was 0·2708. From these numbers determine the density of ozone (a) with chlorine as unity and (b) with hydrogen as unity.

Ans. (a) 0·7025, (b) 24·94.

Problem 28. The value of pv at 0°C. and one atomsphere taken as unity, in the case of oxygen, becomes at 0°C. and 0·5 atmosphere, 1·00047 (O_2.). Assuming that α remains uniform down to $p = 0$, find the relative density (d_0) of oxygen at zero pressure, if d at N. T. P. is 15·90.

Ans. 15·89.

Problem 29. In the case of gaseous HCl $pv = 54{,}803$ and $p_0v_0 = 55{,}213$. The weight of a litre of HCl at N. T. P. being 1·63915, what is the molecular weight of HCl? (O_2 = 32, limiting density of O_2 = 1·4276).

Ans. 36·49.

Problem 30. Cawood and Patterson give the following results for the normal densities and effective compressibility coefficients.

Gas	Normal Density	$1 + \gamma$
Ethylene	1·2606	1·0073
Carbon dioxide	1·9767	1·0066
Nitrous oxide	1·9777	1·0071
Sulphur dioxide	2·9265	1·0249
Dimethyl ether	2·1100	1·0281.

Calculate the molecular weight of these compounds, and the atomic weights of carbon, nitrogen and sulphur.

Ans. Molecular Weights: Ethylene 28·05; Carbon dioxide 44·015; Nitrous oxide 44·016; Sulphur-di-oxide 64; Dimethyl ether 46·001.

Atomic weights:	Carbon	12·010	from	Ethylene
	,,	12·015	,,	Carbon dioxide
	,,	11·98	,,	Dimethyl ether
	Nitrogen	14·008		
	Sulphur	32·00.		

Problem 31. Given that the solubilities of I_2 in water and CS_2 are respectively 1 to 590, and that the mole. condition of I_2 is the same in both. What will be the weight of I_2 left in one litre of an aqueous I_2 solution, originally at 18°C. after having been shaken with 100 c. c. of CS_2? Solubility of I_2 at 18°C. = 1 gram in 3636 of water.

Ans. 0·00460 gm.

Problem 32. Show from the following data that the molecules of formic acid in the liquid state, are associated, but they gradually dissociate as the temperature rises.

Radius of capillary = 0·01425 cm.

Temperature :	16·8	46·4	79·1°C
Height of liquid :	4·442	4·205	3·90 cm.
Density :	1·207	1·170	1·129

Ans. The molecular weight calculated from first two determinations = 160, and that from the last two = 145. The theoretical molecular weight of formic acid is 46.

Problem 33. From the following data determine the molecular weight of liquid nitrogen peroxide. Liquid nitrogen peroxide rises to a height of 3·14 cms. at 1·6°C. in a capillary tube of 0·0129 cm radius, and to a height of 2·905 cms. in the same tube at 19·8°C. The density of the peroxide is 1·486 at 1·6°C. and 1·444 at 19·8°C.

Ans. Formula for nitrogen peroxide is N_2O_4 and the molecular weight is 92.

Problem 34. In the case of formic acid, the increase in the molecular surface tension between 16·1°C. and 46·4°C. was found to be 0·902 per 1°, and between 46·4°C. and 79·8°C., 0·991 per 1°.

If the mean constant for the non associated liquids is 2·121, find the mean degree of association (x) over the two intervals of temperatures.

Ans. x = 3·605 between 16·1°C. and 46·4°C.;

x = 3·131 between 46·4°C. and 79·8°C.

Problem 35. The surface tension of chloroform (density = 1·526 gm/c. c.) is 27·2 dynes per cm. Calculate its parachor and compare it with the theoretical value.

Ans. Calculated = 178·8; theoretical = 184·8.

Problem 36. The surface tension of benzene is 29·2 dynes/cm. and its density is 0·88 gm/c. c. Calculate its parachor and compare it with the theoretical value.

Ans. Calculated = 206; theoretical = 206·1.

Problem 37. What is the surface tension of water at 4°C. ? Atomic parachor for hydrogen is 17·1, and atomic parachor for oxygen is 20·0.

Ans. 82·19 dynes per cm.

CHAPTER II

THERMODYNAMICS AND THERMOCHEMISTRY

12. **First Law of Thermodynamics** :—The different kinds of energy in an isolated system are capable of being mutually transformed wholly or partially; but the sum total of the energy in the system remains constant. This is the principle of the conservation of energy. The first law of thermodynamics based on this, emphasises the quantitative interconvertibility of heat and mechanical energy.

If U is the energy of a system, and if it absorbs isothermally and reversibly an amount of heat (Q) and performs work (A) due to expansion against external pressure, then,

$$dU = dQ - dA \text{ or, } dQ = dU + dA$$

where dU represents the *increase* in the energy of the system, dQ the heat absorbed, and dA the work done.

If the system evolves (*i e.* loses) an amount of heat (Q) and the work done on the system is (A) then,

$$dU = dA - dQ$$

where dU represents the *decrease* in the energy of the system, dA the work done on the system, and dQ the heat lost by the system.

In a chemical reaction, when heat is evolved, the system becomes poorer by that much amount of energy, and the evolved heat should be shown as $-$ *ve*, while, if heat is absorbed by the system, it becomes richer by that much amount of energy, and the heat absorbed should be shown as $+$ *ve*.

Important applications of the first law of thermodynamics:—

(i) The heat evolved in a reaction, depends only on the initial and the final conditions of the system, and not on the stages in which the final condition is reached. It is, therefore, constant, whether the reaction occurs in one step or in a series of

steps This is the Law of Hess. It enables one to determine the heat of formation of substances, which may not be capable of being conveniently determined by direct experiments. Knowing for example, the heat of combustion of carbon, hydrogen, and marsh gas, the above law enables us to determine the heat of formation of marsh gas.

(ii) First law of thermodynamics makes it possible to determine the maximum work done, during an isothermal expansion of a gas, provided, the expansion is carried out in a perfectly reversible manner.*

If the expansion occurs between the limits V_2 and V_1, at a pressure p, the maximum work (A) done is :—

$$A = \int_{v_1}^{v_2} P dv, \text{ but, } P = \frac{nRT}{V}$$

$$A = \int_{v_1}^{v_2} nRT \frac{dv}{V}$$

$$= nRT \log_e \frac{V_2}{V_1}$$

$$= 2{\cdot}302\ nRT \log \frac{V_2}{V_1}.$$

If $n = 1$,

$$A = 2{\cdot}302\ RT \log \frac{V_2}{V_1}.$$

or, $$= 2{\cdot}302\ RT \log \frac{P_1}{P_2}.$$

(iii) The determination of the relation of specific heats [$Cv = 3$ cals., and $Cp - Cv = R \approx 2$ cals.], and that of heat capacities of a system, are based on the first law of thermodynamics. The energy of a perfect gas, assuming it to be all translational in character, is $\frac{nmc^2}{2}$, where c is the velocity of the gas. Then,

* A reversible reaction in thermodynamic sense is one which can be made to occur in either direction. This is only possible if the conditions governing the equilibrium undergo an infinitesimal change during the reaction.

$$PV = \frac{1}{3} nmc^2$$

$$\therefore \quad PV = \frac{2}{3} \cdot \frac{nmc^2}{2}$$

As c depends on temperature, P varies as T, and is constant for a given temperature. A gram molecule, at a definite temperature and pressure, occupies a definite volume; and PV = RT for a gram molecule, the value of R being approximately 2 cals.

$$\text{Now,} \quad PV = \frac{2}{3} \cdot \frac{nmc^2}{2}. \qquad \therefore \frac{2}{3} \cdot \frac{nmc^2}{2} = RT.$$

$\therefore \dfrac{nmc^2}{2}$ (kinetic energy of the gram molecule of the gas)

$$= \frac{3}{2} RT.$$

At T_2, $(PV)_{T_2} = \frac{3}{2} RT_2$, and at T_1, $(PV)_{T_1} = \frac{3}{2} RT_1$.

The difference in the kinetic energy of a gram molecule of a gas, between T_2 and T_1 is $\frac{3}{2} R (T_2 - T_1)$.

If, $T_2 - T_1$ = one, the difference in the kinetic energy of a gram molecule at constant volume is $\frac{3}{2}$ R, and, as $R \approx 2$, C_v (for a pefect gas) = 3 cals.

If, as the temperature increases, the volume is allowed to increase at constant pressure, the work done is $Pdv = 2$ cals.

$$\therefore C_p - C_v = 2 \text{ cals. for a perfect gas.}$$

(iv) The relation between P and V in an adiabetic expansion, is based on a relation $dU = dA + dQ$. Heat is not supplied to the system during an adiabetic expansion, and so, $Q = 0$, $\qquad \therefore dU = dA$.

The work done during such an expansion has to use the energy of the system. There is, consequently, a fall of tempera-

ture dt, and if C_v is the specific heat at constant volume, the heat utilised during expansion is :

$$dA = C_v dt, \qquad \text{but, } dA = P dv$$

$$\therefore \quad P dv = C_v dt.$$

But for a gram molecule, $P = \frac{RT}{V}$

$$\therefore \quad RT \frac{dv}{V} = C_v dt.$$

Integrating between V_2 and V_1 and T_1 and T_2,

$$R \log_e \frac{V_1}{V_2} = C_v \log_e \frac{T_2}{T_1};$$

$$\text{but, } R = C_p - C_v,$$

$$\therefore \quad (C_p - C_v) \log_e \frac{V_1}{V_2} = C_v \log_e \frac{T_2}{T_1},$$

$$\therefore \quad \frac{C_p - C_v}{C_v} \log_e \frac{V_1}{V_2} = \log_e \frac{T_2}{T_1}.$$

$$\text{If, } \frac{C_p}{C_v} \text{ is taken } = \gamma,$$

$$(\gamma - 1) \log_e \frac{V_1}{V_2} = \log_e \frac{T_2}{T_1}$$

$$\left(\frac{V_1}{V_2}\right)^{\gamma - 1} = \frac{T_2}{T_1};$$

$$T_1 (V_1)^{\gamma - 1} = T_2 (V_2)^{\gamma - 1}.$$

But, $T_1 = \frac{P_1 V_1}{R}$ and $T_2 = \frac{P_2 V_2}{R}$

$$\therefore \quad \frac{P_1 V_1}{R} (V_1)^{\gamma - 1} = \frac{P_2 V_2}{R} (V_2)^{\gamma - 1}$$

$$P_1 (V_1)^{\gamma} = P_2 (V_2)^{\gamma}$$

$$\therefore \quad \frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}.$$

(v) An explanation of the Joule Thomson effect can be obtained by the application of the first law of thermodynamics. As PV is constant, the energy of an ideal gas should be independent of its volume. Most of the gases, however, if compressed and then allowed to diffuse into a chamber kept at a low pressure, become colder (Joule Thomson effect). The particles of an ideal gas do not exert any attraction on one another, and further, the actual volume that the particles occupy is so small, that it may be taken as zero. But the particles of gases generally possess some attraction for one another, and the actual volume that the particles occupy cannot be taken as zero, except at a very low pressure. Further, in gases which are not monoatomic, work has to be done to overcome the attraction between their component atoms during expansion.

If PV is plotted against pressure, for an ideal gas, the graph should be a horizontal line (Fig. 1). In the case of ordinary gases (like O_2, N_2 etc.) there is a decrease in the value of PV at moderate pressures, and at high pressures there is an increase in the value of PV, while, in the case of H_2, He, at ordinary temperature there is no decrease in the value of PV (even at moderate pressures,) but, a continuous increase in the value of PV. Van der Waals introduced the constants *a* and *b* in the gas equation to explain the above behaviour.

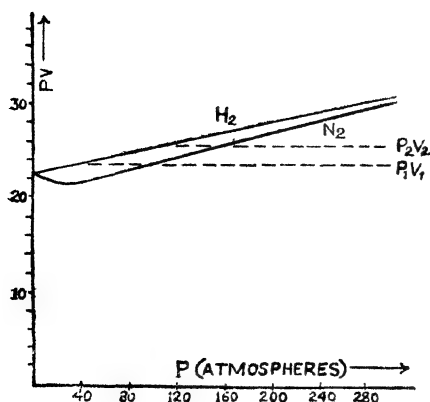



Fig. 1

If an ideal gas is compressed to a high pressure at ordinary temperature, and then allowed to expand without doing any external work, it should not change its temperature. Gases like O_2, N_2 etc. under such conditions become cooler (Joule Thomson effect), while, He and H_2 under similar conditions get slightly

warmer. With gases O_2 and N_2, as the gas is compressed at moderate pressure, and allowed to expand, P_1 being $< P_2$ and P_1V_1 being greater than P_2V_2, the gas does work. At the same time as $V_1 > V_2$ it does work in overcoming the attraction between the particles of the gas;* and both these effects produce a lowering in temperature.

When a gas like O_2 compressed at a high pressure, is allowed to expand, P_1V_1 being less than P_2V_2, work is done on the gas; but V_1 being greater than V_2, it also does internal work as before. First effect makes the gas hotter, but it is more than counterbalanced by the second effect, and the temperature of the gas therefore gets lowered.

In the case of H_2, the first effect predominates over the second effect, and the gas gets hotter when expanded at ordinary temperature.

If, however, H_2 is previously cooled by liquid air to about $-70°C$. (inversion temperature) the second effect predominates over the first one, as in the case of O_2 and N_2, and H_2 also gets cooled on expansion. Linde's method to liquefy O_2, N_2 and H_2 (initially cooled by liquid air) is based on the above effect.

13. Thermo-Chemistry.—

Important formulæ :—

(1) Hess's Law, (2) Heat at constant volume and at constant pressure.

(1) *Hess's Law*:—The heat of a chemical reaction for a given quantity of the reacting substances is the same, whether the reaction takes place in one or several stages.

(2) The relation of heat at constant volume and heat at constant pressure (of a chemical reaction) is given by the equation

* There is also in the case of di or poly atomic gases the possibility of work being done in expansion in overcoming the attraction between the component atoms of the molecules.

$$Qv = Qp + nRT$$

where, Qv = the heat at constant volume
Qp = ,, ,, ,, ,, pressure
n = number of mols (gas) in the final state in excess of the number of mols (gas) in the initial state.
R = constant expressed in calories, *i. e.*, 1·985.
T = Absolute temperature at which the reaction takes place.

14. **Change of State.**—1. Variation of the temperature of fusion with pressure can be calculated by a cyclic method.

At the melting point T, the solid and the liquid have definite vapour pressure P, and are in equilibrium with each other, and the work done in the process of fusion depends on the difference of volume of the solid and the liquid ($V_l - V_s$). The influence of this change in volume can be studied by carrying out the process in a cyclic way represented by a P – V diagram. (Fig. 2)

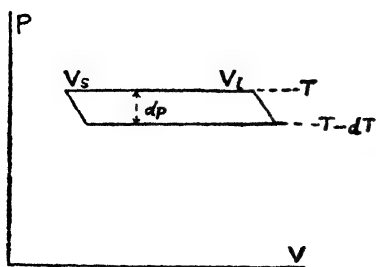



Fig. 2 Clausius Equation
V_s = Volume of solid
V_l = Volume of liquid

(i) Melt *a gram* of the solid at a pressure P and at the corresponding temperature T (the melting point of the solid under pressure P). Heat q (latent heat of fusion l) is absorbed at T. Work W_1 done in the change of V = P ($V_l - V_s$).

(ii) Change the pressure on the liquid to $P - d_p$, and change the temperature to $T - d_t$ (melting point of the solid at $P - d_p$).

(iii) Change the liquid into the solid at the pressure $P - d_p$ and the temperature $T - d_t$. Heat q is evolved, at $T - d_t$ and the work W_2 done in the change in volume is

$$(P - d_p)(V_s - V_l).$$

(iv) Change the pressure on the solid from $P - d_p$ to P and change the temperature from $T - d_t$ to T to restore the original condition.

Stages ii and iv approximately cancel each other.

In (i) heat q is absorbed at the temperature T and in (iii) heat q is liberated at the temperature $T - dt$, while the net work dw due to change in volume is $W_1 + W_2$.

$$\begin{aligned} dw &= W_1 + W_2 \\ &= P(V_l - V_s) + (P - dp)(V_s - V_l) \\ &= P(V_l - V_s) - (P - dp)(V_l - V_s) \\ &= dp(V_l - V_s). \end{aligned}$$

This is the area of the parallelogram in P – V diagram.

$$\text{But,} \quad dw = q\frac{dT}{T}$$

$$\therefore \quad dp(V_l - V_s) = q\frac{dT}{T}$$

or

$$\frac{dT}{dp} = \frac{T(V_l - V_s)}{q}$$

This is called the equation of 'Clausius'.

It should be noted that if V_s is greater than V_l (as in the case of water) $V_l - V_s$ is negative and dT and dp have opposite signs. The melting point falls with rise of pressure in such a case.

2. Variation of pressure with temperature in the process of vaporisation.

At a given temperature T, a liquid has a definite vapour pressure, and the liquid and its vapour are in equilibrium. The work done in the process of evaporation depends on the difference in volume of the liquid and that of the vapour in which it is converted. The influence of this change in volume on the relation between pressure and temperature, can be studied by a P – V diagram as in the process of fusion.

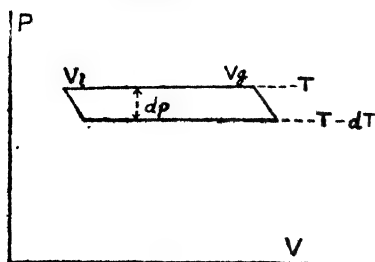



Fig. 3

V_l = Volume of the liquid

V_g = Volume of the vapour in which it is converted.

(i) Vaporise *a gram molecule* of a liquid having a volume V_l at a pressure P and the corresponding temperature T and the vapour formed has a volume V_g.

q, the molecular latent heat of evaporation L, is absorbed at the temperature T and the work W_1 done in the change of volume is $P(V_g - V_l)$.

(ii) Change the pressure to $P - dp$ and change the temperature to $T - dT$ (corresponding temperature).

(iii) Condense the vapour V_g to liquid V_l at the temperature $T - dT$. q, molecular latent heat of evaporation L, evolved at the temperature $T - dT$, and work W_2 done, in the change of volume is $(P - dp)(V_l - V_g)$.

(iv) Change the pressure on the liquid from $P - dp$ to P and change the temperature from $T - dT$ to T to restore the original condition.

Stages (ii) and (iv) approximately cancel each other. In (i), heat q is absorbed at the temperature T and in (iii), heat q is evolved at the temperature $T - dT$, while the net work done $dw = W_1$ [the work done in the change in volume at $P = P(V_g - V_l)$] $+ W_2$, [the work done in the change in volume at $P - dp = (P - dp)(V_l - V_g)$]

$$\begin{aligned} dw &= W_1 + W_2 \\ &= P(V_g - V_l) + (P - dp)(V_l - V_g) \\ &= P(V_g - V_l) - (P - dp)(V_g - V_l) \\ &= dp(V_g - V_l). \end{aligned}$$

$$\text{But,} \quad dw = q\frac{dT}{T}$$

$$\therefore \quad dp(V_g - V_l) = q\frac{dT}{T}.$$

$$\therefore \quad \frac{dp}{dT} = \frac{q}{T(V_g - V_l)} \approx \frac{q}{T \cdot V_g}$$

V_l being very small compared to V_g, can be neglected. Assuming that the vapour follows gas laws,

$$PV_g = RT \text{ or } V_g = \frac{RT}{P}$$

$$\therefore \quad \frac{dp}{dT} = \frac{q}{T \times RT \times \frac{1}{P}}$$

$$\therefore \quad \frac{1}{P} \cdot \frac{dp}{dT} = \frac{q}{RT^2}$$

$$\therefore \quad d \log P = \frac{qdT}{RT^2}$$

$$\therefore \quad \int d \log P = \frac{q}{R} \int \frac{dT}{T^2}$$

Integrate between P_1 and P_2 and, T_1 and T_2

$$\log P_1 - \log P_2 = \frac{q}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

P_1 and P_2 are pressures at T_1 and T_2 and q is the heat of the reaction.

If S_1 and S_2 are the solubilities at T_1 and T_2 and q is the heat of solution, a similar expression:—

$\log S_1 - \log S_2 = \frac{q}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$ gives relation between these magnitudes.

15. **Second Law of Thermodynamics.**— If a system changes from A to B, the First Law states that the total energy remains constant. It does not define the conditions under which such a change can occur. Second Law of Thermodynamics specifies these conditions.

1. No such change can occur, unless there is a difference in level, or, there is a gradient. Transfer of heat from a hot body can only occur, if it is brought in contact with a cold one. A flow of electric energy from A to B can only occur when a body A at a higher potential is connected with a body B at a lower potential.

2. No such difference of level could be produced artificially. No machine has been devised which can separate the vast amount of heat present in water of oceans into one portion at a higher temperature, and another at a lower temperture, and obtain work by allowing them to equalise.

3. Maximum amount of work in such transfers can only be obtained if the transfer is made to occur in a perfectly reversible manner. As most spontaneous processes are irreversible, or not

completely reversible, whole or part of the energy is transferred into heat and maximum amount of work is not obtained. Since our environments are not at zero level with respect to heat energy, part only of the heat so produced can again be converted into work.

The Second Law of Thermodynamics thus shows that in all transfers of energy, some part of the energy, which is already converted into heat becomes incapable of being again completely utilised. The Law is sometimes, therefore, defined as the Principle of the Degradation of Energy.

Carnot's Theorem gives the maximum amount of work obtained during the conversion of heat into work under perfectly reversible conditions by a cyclic process.

The conversion of heat may be supposed to occur in four stages, an ideal gas being the working substance.

(1) Isothermal expansion of one mol of the gas at temperature T_2 from volume v_1 to volume v_2 is carried out, when Q heat is withdrawn at T_2 from the reservoir.

According to the First Law :—

$$A' = RT_2 \log_e \frac{v_2}{v_1}$$

A′ being the work done by the gas by absorbing Q at T_2.

(2) The expanded gas is then further allowed to expand adiabatically to v_3, its temperature falling to T_1

(3) Isothermal compression to v_4 is then done, when Q heat is given to reservoir at T_1,

$A'' = RT_1 \log_e \frac{v_3}{v_4}$, A″ being the work done on the gas, being equal to heat Q given back at T_1.

(4) The gas finally compressed adiabatically from v_4 to v_1 when the temperature rises to T_2. Cycle is complete and the gas is brought to the initial state.

Since, stages (2) and (4) are adiabatic, there is no energy change in the system during these two stages. In (1) heat Q is

absorbed from the reservoir at T_2 and in (3) heat Q is given back at T_1. The net amount of external work,

$$dA = A' - A''$$

$$= RT_2 \log_e \frac{v_2}{v_1} - RT_1 \log_e \frac{v_3}{v_4}.$$

(5) From the adiabatic changes occurring in (2) and (4)

$$T_2 v_2^{\gamma-1} = T_1 v_3^{\gamma-1},$$

$$T_2 v_1^{\gamma-1} = T_1 v_4^{\gamma-1}$$

$$\therefore \quad \frac{v_2}{v_1} = \frac{v_3}{v_4}$$

$$dA = RT_2 \log_e \frac{v_2}{v_1} - RT_1 \log_e \frac{v_2}{v_1}$$

$$= R(T_2 - T_1) \log_e \frac{v_2}{v_1}.$$

Expressing the output of work as a fraction of the work, 'A' being equal to the heat Q absorbed at T_2, one gets

$$\frac{dA}{Q} = \frac{R(T_2 - T_1) \log_e \frac{v_2}{v_1}}{RT_2 \log_e \frac{v_2}{v_1}}$$

$$= \frac{T_2 - T_1}{T_2}.$$

If the temperature difference $T_2 - T_1$ is very small, it can be expressed as ΔT and the work as ΔA and,

$$\frac{\Delta A}{Q} = \frac{\Delta T}{T}$$

$$\text{or,} \quad Q = T\frac{\Delta A}{\Delta T} \text{ or } T\frac{dA}{dT}.$$

Gibb's Helmholtz Equation.— According to the First Law of Thermodynamics

$$U = A - Q$$

U being the change in the energy of a system, A, the work done and Q the heat evolved.

$$\therefore \quad A - U = Q$$

and according to the Second Law of Thermodynamics

$$Q = T \frac{dA}{dT}$$

$$\therefore \quad A - U = T\frac{dA}{dT}$$

Problems with solutions

Problem 38. The adiabatic compression of a mixture of $2H_2 + O_2$ from 377 c. c. to 30·7 c. c. caused explosion; the initial temperature was 18°C. and initial pressure 1 atmosphere. Calculate the temperature of the explosion and the pressure at the moment of its occurrence ($\gamma = 1{\cdot}4$).

Solution : Calculate the pressure at the moment of explosion using the formula

$$PV^{\gamma} = P_1V_1{}^{\gamma}$$

$$i.e., \quad 1 \times 0{\cdot}377^{1\cdot4} = P_1 \times 0{\cdot}0307^{1\cdot4}$$

$$P_1 = \left(\frac{0{\cdot}377}{0{\cdot}0307}\right)^{1\cdot4}$$

$$= (12{\cdot}27)^{1\cdot4}$$

$$= 33{\cdot}51 \text{ atmospheres.}$$

The formula $\left(\frac{v_2}{v_1}\right)^{\gamma - 1} = \frac{291}{T_2}$

gives the temperature of explosion

$$\left(\frac{0{\cdot}0307}{0{\cdot}377}\right)^{0\cdot4} = \frac{291}{T_2}$$

$$T_2 = 291 \times \left(\frac{0{\cdot}377}{0{\cdot}0307}\right)^{0\cdot4}$$

$$= 793{\cdot}6.$$

Ans. 520·6°C; 33·51 atmos.

Problem 39. Calculate the change in temperature corresponding to a pressure difference of one atmosphere (the Joule-Thomson effect) for oxygen at 0°C. $a = 1{\cdot}36$; $b = 0{\cdot}0316$; $RT = 22{\cdot}4$. Taking 1 litre as the unit of volume; $C_p = 6{\cdot}9$.

Solution : The change in temperature is given by the equation

$$K = \frac{\frac{2a}{RT} - b}{C_p} \times 24{\cdot}1$$

$$T_2 - T_1 = \text{fall in temperature} = \left(\frac{2{\cdot}72}{22{\cdot}4} - 0{\cdot}0316\right)\frac{24{\cdot}1}{6{\cdot}9}$$
$$= 0{\cdot}31.$$

Ans. 0·31.

Problem 40. Calculate the temperature (the inversion temperature) below which there will be a cooling effect (on lowering of pressure) in the case of hydrogen. $a = 0{\cdot}19$; $b = 0{\cdot}023$; $C_p = 6{\cdot}9$.

Solution : Change in temperature is given by the equation

$$K = \left(\frac{2a}{RT} - b\right) \times \frac{24{\cdot}1}{C_p}$$

At the temperature (point of inversion) the value of K changes sign *i. e.*, it vanishes.

$$\therefore \quad \frac{2a}{RT} - b = 0$$

$$i.e. \quad \frac{2a}{RT} = b$$

$$\therefore \quad 2a = RTb$$

$$T = \frac{2a}{Rb}$$

$$= \frac{0{\cdot}38}{0{\cdot}082 \times 0{\cdot}023}$$

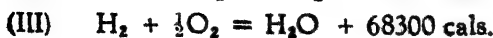
$$= 201{\cdot}5 \quad \text{or} \quad -71{\cdot}5°\text{C}.$$

Ans. − 71·5°C.

Problem 41. Calculate the heat of formation of CH_4 from the following data :—

(I) $CH_4 + 2O_2 = CO_2 + 2H_2O + 213800$ cals.

(II) $C + O_2 = CO_2 + 94300$ cals.

(III) $H_2 + \frac{1}{2}O_2 = H_2O + 68300$ cals.

Solution : Subtract (I) from (II) and add twice (III) :

$$(C + O_2 - CH_4 - 2O_2) + 2(H_2 + \tfrac{1}{2}O_2)$$

$$= CO_2 - CO_2 - 2H_2O + 94300 - 213800 + 136600 + 2H_2O$$

i. e. $C + 2H_2 = CH_4 + 17100$ cals.

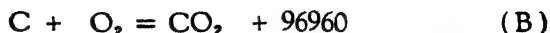
Ans. The heat of formation of CH_4 is 17100 cals.

Problem 42. The heat of formation of liquid water is 68360 cals. and of carbon dioxide 96960 cals. both at 17°C. and at constant pressure. The heat of combustion of ethane under the same conditions is 370440 cals. Calculate the heat of formation of ethane at 17°C. (*a*) at constant pressure and (*b*) at constant volume.

Solution :

$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68360 \qquad (A)$$

$$C + O_2 = CO_2 + 96960 \qquad (B)$$

$$C_2H_6 + \tfrac{7}{2}O_2 = 2CO_2 + 3H_2O + 370440 \qquad (C)$$

Multiply A by 3 and B by 2, and add them together. Subtract C from this sum.

$$3H_2 + \tfrac{3}{2}O_2 + 2C + 2O_2 - C_2H_6 - \tfrac{7}{2}O_2$$

$$= 3H_2O + 2CO_2 + 3 \times 68360 - 3H_2O - 2CO_2 + 2 \times 96960 - 370440$$

$$3H_2 + 2C - C_2H_6 = 205080 + 193920 - 370440$$

$$2C + 3H_2 = C_2H_6 + 28560 \text{ cals. at constant pressure.}$$

To find the heat of formation at constant volume, use the equation

$$Q_v = Q_p + nRT$$

$$= 28560 - 2 \times 1{\cdot}985 \times 290$$

$$= 28560 - 1153$$

$$= 27407 \text{ cals. at constant volume.}$$

Ans. The heat of formation of ethane at

(a) constant pressure is 28560 cals., and at

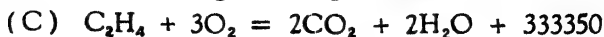
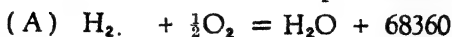
(b) constant volume is 27407 cals.

Problem 43. The heat of formation of liquid water is 68360 cals. and that of carbon dioxide 96900 cals. both at 14°C. and at constant pressure. The heat of combustion of ethylene under the same conditions 333350 cals. Calculate the heat of formation of ethylene at 14°C; (a) at constant pressure and (b) at constant volume.

Solution : The reactions are represented as follows :—

$$(A)\quad H_2 + \tfrac{1}{2}O_2 = H_2O + 68360$$

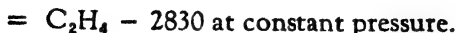
$$(B)\quad C + O_2 = CO_2 + 96900$$

$$(C)\quad C_2H_4 + 3O_2 = 2CO_2 + 2H_2O + 333350$$

Multiplying A and B by 2 and deducting C from their sum (2A + 2B − C) we get,

$$2H_2 + 2C + 3O_2 - C_2H_4 - 3O_2$$

$$= 2H_2O + 2CO_2 - 2CO_2 - 2H_2O + 136720 + 193800 - 333350$$

$$2H_2 + 2C = C_2H_4 + 330520 - 333350$$

$$= C_2H_4 - 2830 \text{ at constant pressure.}$$

To find the heat at constant volume, use the equation

$$Qv = Qp + nRT$$

$$Qv = -2830 - 1 \times 1{\cdot}985 \times 287$$

$$= -3349.$$

Ans. The heat of formation of ethylene at

(a) constant pressure = − 2830 cals., and at

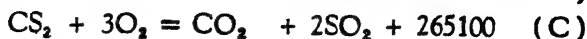
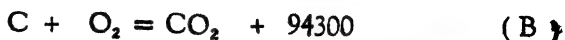
(b) constant volume = − 3349 cals.

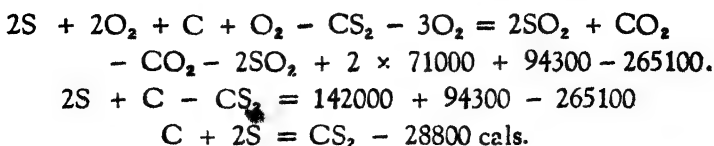
Problem 44. The heat of formation of SO_2 and CO_2 are respectively 71000 and 94300 cals. and the heat of combustion of CS_2 is 265100 cals. Calculate the heat of formation of CS_2.

Solution :

$$S + O_2 = SO_2 + 71000 \qquad (A)$$

$$C + O_2 = CO_2 + 94300 \qquad (B)$$

$$CS_2 + 3O_2 = CO_2 + 2SO_2 + 265100 \qquad (C)$$

Multiply A by 2, and add it to B; then subtract C from their sum.

$$2S + 2O_2 + C + O_2 - CS_2 - 3O_2 = 2SO_2 + CO_2$$
$$- CO_2 - 2SO_2 + 2 \times 71000 + 94300 - 265100.$$
$$2S + C - CS_2 = 142000 + 94300 - 265100$$
$$C + 2S = CS_2 - 28800 \text{ cals.}$$

Ans. The heat of formation of CS_2 is $-$ 28800 cals.

Problem 45. The heat of combustion of carbon monoxide is 68000 cals. while that of hydrogen is 68380 cals. Calculate the calorific value in cals. per litre (at N. T. P.) of a water gas containing 50 per cent. hydrogen, 44 per cent. carbon monoxide, 3 per cent. carbon dioxide and 3 per cent. nitrogen by volume.

Solution : The percentages of carbon dioxide and nitrogen have no significance in calculating the calorific value. They may be neglected. One litre of the water gas contains 0·5 litre of hydrogen and 0·44 litre of carbon monoxide, or, $\frac{0 \cdot 5}{22 \cdot 4}$ mols of hydrogen, and $\frac{0 \cdot 44}{22 \cdot 4}$ mols of carbon monoxide. The heats liberated by them on combustion will be,

$$\text{by hydrogen } \frac{0 \cdot 5}{22 \cdot 4} \times 68380 = 1526 \text{ cals.}$$

$$\text{and by carbon monoxide } \frac{0 \cdot 44}{22 \cdot 4} \times 68000 = 1336 \text{ cals.}$$

The total heat liberated will be

$$1526 + 1336 = 2862 \text{ cals.}$$

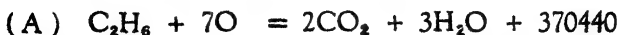
Ans. The calorific value of water gas per litre (N. T. P.) is 2862 cals.

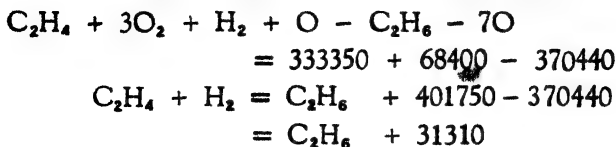
Problem 46. The heat of combustion of ethane, ethylene and hydrogen are respectively 370440, 333350, and 68400 cals. Calculate the energy change when ethylene is reduced to ethane.

Solution : The reactions of combustion are as follows :

(A) $C_2H_6 + 7O = 2CO_2 + 3H_2O + 370440$

(B) $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O + 333350$

(C) $H_2 + O = H_2O + 68400$

Add B and C, and subtract A from the sum.

$$C_2H_4 + 3O_2 + H_2 + O - C_2H_6 - 7O$$
$$= 333350 + 68400 - 370440$$
$$C_2H_4 + H_2 = C_2H_6 + 401750 - 370440$$
$$= C_2H_6 + 31310$$

Ans. 31310 cals. are liberated.

Problem 47. Expressing the weights of carbon and steam in kilograms and quantities of heat in kilogram calories the following are the thermo-chemical equations for the reactions in a gas producer.

$$\frac{1}{12}\left(C + O_2 \right) = \frac{1}{12}\left(CO_2 \right) + 8100 \text{ kg. calories.}$$

$$\frac{1}{12}\left(C + \tfrac{1}{2}O_2 \right) = \frac{1}{12}\left(CO \right) + 2430 \text{ kg. calories.}$$

$$\frac{1}{18}\left(H_2O \right) \text{ steam} = \frac{1}{18}\left(H_2 + \tfrac{1}{2}O_2 \right) - 3196 \text{ kg. cals.}$$

It is estimated that in a large producer, 10 per cent. of the total calorific value of fuel is required to balance losses by radiation, etc. How much steam, therefore, can be decomposed by each kilogram of carbon burnt.

Solution : The total calorific value of the fuel (in kilogram calories) is 8100 kilogram calories; the heat required to balance the losses by radiation is 810 kg. cals. The heat available for the decomposition of steam is,

$$2430 - 810 = 1620 \text{ kg. cals.}$$

because in a producer, C is burnt to CO only, and the heat is produced to the extent of 2430 kg. cals. per kg. of C burnt.

The amount of steam decomposed will be,

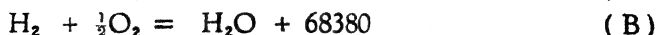
$$\frac{1620}{3196} = 0{\cdot}5069 \text{ kg.}$$

Ans. 0·5069 kg. of steam will be decomposed by each kilogram of carbon burnt.

Problem 48. The heat of formation of CO_2 and H_2O are respectively 94380 and 68380 cals., and the heat of combustion of

propane is 526300 cals. The heat of rupture of C—H is 93600 cals. Calculate the heat of rupture of C—C linkage.

Solution : First find the heat of formation of propane,

$$C + O_2 = CO_2 + 94380 \quad (A)$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68380 \quad (B)$$
$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O + 526300 \quad (C)$$

Multiplying A by 3, and B by 4 and subtracting C from their sum, the heat of formation of propane is,

$$\left.\begin{array}{l} 94380 \times 3 = 283140 \\ 68380 \times 4 = 273520 \end{array}\right\} = 556660 - 526300 = 30360$$

The heat of formation does not include the heat of atomization of the elements. The heat of formation of propane from its constituent atoms will be the heat of formation as found above plus the heat of atomization of elements *i. e.*, C and H.

The atomic heat of formation = The heat of formation + The heats of atomization of the elements.

$$= 30360 + 3 \times 150000 + 8 \times 51500$$
$$= 892360 \text{ cals.}$$

In propane there are 8 C—H linkages and 2 C—C linkages; subtracting the heat of rupture of C—H linkages from the atomization heat of formation, and dividing the remainder by 2 will give the heat of rupture of C—C linkages.

$93600 \times 8 = 748800$ cals. heat of rupture of 8 C—H linkages.

$$\frac{892360 - 748800}{2} = 71780 \text{ cals.}$$

Ans. The heat of rupture of C—C linkage is 71780 cals.

Problem 49. The atomic heats of formation of benzene and naphthalene are 1193·2 and 1881·5 kg. cals. per gram molecule respectively. Calculate the heats of rupture of the C—C, and C–H linkages in aromatic compounds, benzene and naphthalene.

Solution : In benzene there are 6 C—C linkages and as many C—H linkages. In naphthalene they are 11 and 8 respectively.

If x be the heat of rupture of C—C linkage and y be that of C—H linkage, then

$$6x + 6y = 1193{\cdot}2 \qquad (I)$$
$$11x + 8y = 1881{\cdot}5 \qquad (II)$$

Multiplying (I) by 8 and (II) by 6 and subtracting the first from the second, we get,

$$48x + 48y = 1193{\cdot}2 \times 8$$
$$66x + 48y = 1881{\cdot}5 \times 6$$
$$18x = 1743{\cdot}4$$
$$x = 96{\cdot}855 \text{ kg. cals.}$$

From (I) $x + y = 198{\cdot}866$

$$y = 198{\cdot}866 - 96{\cdot}855$$
$$= 102{\cdot}011 \text{ cals.}$$

Ans. The heat of rupture of C—C is 96·855 kg. cals.
,, ,, ,, ,, of C—H is 102·011 kg. cals.

Problem 50. The heat of reaction :

$$K + H_2O + aq = KOHaq + \tfrac{1}{2}H_2 \text{ is 48000 cals.}$$

How much potassium must be added to 100 grams of water at 15°C. in order to make it boil, assuming that 60 per cent. of the heat is absorbed by water.

Solution : The heat required by water to be raised to the boiling point is

$$100\,(100° - 15°) = 100 \times 85$$
$$= 8500 \text{ calories.}$$

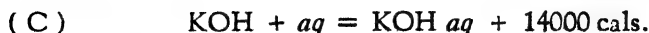
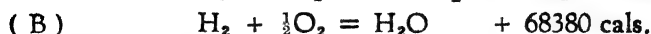
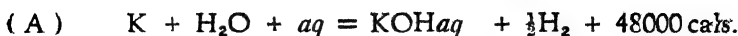
As only 60% of the heat is absorbed by water, the total heat to be generated is $\frac{8500 \times 100}{60} = 14170$. The amount of potassium required to liberate this heat is $\frac{14170 \times 39}{48000} = 11{\cdot}51$ grams.

Ans. 11·51 grams potassium must be added.

Problem 51. Calculate the heat of formation of potassium hydroxide from the following data :—

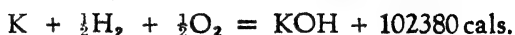
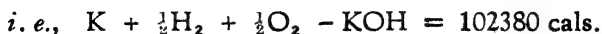
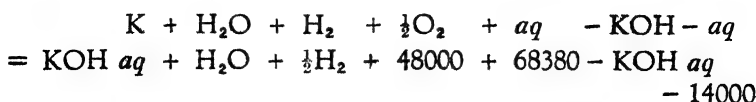
(A) $K + H_2O + aq = KOHaq + \frac{1}{2}H_2 + 48000$ cals.

(B) $H_2 + \frac{1}{2}O_2 = H_2O + 68380$ cals.

(C) $KOH + aq = KOH\,aq + 14000$ cals.

Solution : Add (A) and (B) and deduct (C) from their sum : A + B − C,

$$K + H_2O + H_2 + \frac{1}{2}O_2 + aq - KOH - aq$$
$$= KOH\,aq + H_2O + \frac{1}{2}H_2 + 48000 + 68380 - KOH\,aq - 14000$$

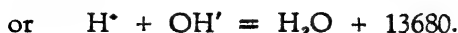
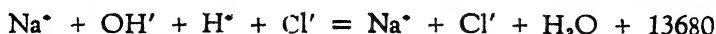
i.e., $K + \frac{1}{2}H_2 + \frac{1}{2}O_2 - KOH = 102380$ cals.

$$K + \frac{1}{2}H_2 + \frac{1}{2}O_2 = KOH + 102380 \text{ cals.}$$

Ans. The heat of formation of KOH is 102380 cals.

Problem 52. The heats of neutralisation of sodium hydroxide and ammonium hydroxide with hydrochloric acid are 13680 and 12270 cals. per gram mol respectively. Assuming that ammonium hydroxide is practically undissociated, calculate its heat of dissociation.

Solution : $NaOH + HCl = NaCl + H_2O + 13680$ (I)

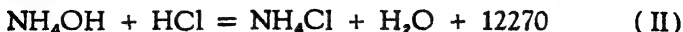
Assuming that NaOH, HCl and NaCl are completely dissociated, the above equation can be written as

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O + 13680$$
or $$H^{\cdot} + OH' = H_2O + 13680.$$

In the equation of neutralization of ammonium hydroxide by hydrochloric acid,

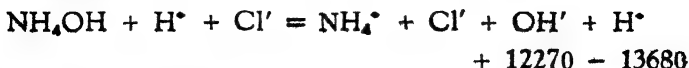
$$NH_4OH + HCl = NH_4Cl + H_2O + 12270 \qquad \text{(II)}$$

HCl can be written as $H^{\cdot} + Cl'$

NH_4Cl can be written as $NH_4^{\cdot} + Cl'$

H_2O can be written as $H^{\cdot} + OH' - 13680$ from above.

The equation II then assumes the form

$$NH_4OH + H^{\cdot} + Cl' = NH_4^{\cdot} + Cl' + OH' + H^{\cdot} + 12270 - 13680$$

$$NH_4OH = NH_4^{\cdot} + OH' - 1410 \text{ cals.}$$

Ans. The heat of dissociation of NH_4OH is − 1410 cals.

Problem 53. The heats of neutralisation of HNO_3 and $CHCl_2COOH$ by NaOH are respectively 13680 cals., and 14830 cals. When one equivalent of NaOH is added to a dilute solution containing one equivalent of HNO_3 and one equivalent of $CHCl_2COOH$, 13960 cals. are liberated. Calculate the relative strengths of the two acids.

Solution : The relative strengths of the two acids are proportional to the equivalent of NaOH neutralised by them.

Let x be the equivalent of NaOH neutralised by HNO_3; then, $1 - x$ will be the equivalent of NaOH neutralised by $CHCl_2COOH$. When neutralised the heat liberated will be,

$$\text{by } HNO_3 = x \times 13680 \text{ cals.}$$

$$\text{and by } CHCl_2COOH = (1 - x) \times 14830 \text{ cals.}$$

$$\text{Then, } x \times 13680 + (1 - x) \times 14830 = 13960.$$

$$i.e., \quad 13680x - 14830x = 13960 - 14830$$

$$-1150x = -870.$$

$$x = 0{\cdot}7565$$

Therefore, 0·7565 mol of NaOH is neutralised by HNO_3 and 0·2435 mol by $CHCl_2COOH$.

$$\text{The relative strength} = \frac{\text{strength of } HNO_3}{\text{strength of } CHCl_2COOH}$$

$$= \frac{0{\cdot}7565}{0{\cdot}2435}$$

$$= \frac{3}{1} \text{ approximately.}$$

Ans. HNO_3 is 3 times stronger than $CHCl_2COOH$.

Problem 54. A molecule of N_2 at 1 atmosphere and 0°C. is used as the working substance in a reversible engine. It is expanded isothermally to three times, and then adiabatically to four times its original volume. It is then compressed isothermally to a certain volume and finally adiabatically to its initial condition. What is the efficiency of the process? ($\gamma = 1{\cdot}4$).

Solution : Let v be the initial volume, the initial temp. $T = 273°$. The work A_1 in the first part of the cycle is,

$$\therefore A_1 = 2{\cdot}3026\ nRT \log \frac{3v}{v}$$

$$= 2{\cdot}3026 \times 1 \times 0{\cdot}08204 \times 273 \times \log \frac{3v}{v}$$

$$= 2{\cdot}3026 \times 0{\cdot}08204 \times 273 \times 0{\cdot}47712$$

$$= 24{\cdot}605 \quad l. \text{ atmospheres.}$$

To calculate A_2, the work in the second part of the cycle the temperature T_2 after adiabatic compression must be known,

$$\left(\frac{v_2}{v_1}\right)^{\gamma - 1} = \frac{T_1}{T_2}$$

$$\left(\frac{4v}{3v}\right)^{0{\cdot}4} = \frac{273}{T_2}$$

$$1{\cdot}122 = \frac{273}{T_2}$$

$$T_2 = \frac{273}{1{\cdot}122}$$

$$= 243{\cdot}2.$$

$$\therefore \quad A_2 = \frac{R\ (T_1 - T_2)}{\gamma - 1}$$

$$= \frac{0{\cdot}08204 \times 29{\cdot}8}{0{\cdot}4}$$

$$= 6{\cdot}112 \quad l. \text{ atmosphere.}$$

The work A_3 in the third part of the cycle is

$$A_3 = 0{\cdot}08204 \times 243{\cdot}2 \times 2{\cdot}3026 \log \frac{v_1}{4v}$$

The value of $\frac{v_1}{v}$ is calculated from the initial (243·2), and the final (273) temperatures of the last part of the cycle.

$$\left(\frac{v_1}{v}\right)^{\gamma - 1} = \frac{273}{243{\cdot}2}$$

$$\frac{v_1}{v} = (1{\cdot}122)^{\frac{1}{0{\cdot}4}}$$

$$= 1{\cdot}3333$$

$$\therefore \quad \frac{v_1}{4v} = 0 \cdot 3333$$

$$\therefore \quad A_3 = -0 \cdot 08204 \times 243 \cdot 2 \times 2 \cdot 3026 \times 0 \cdot 47716$$

$$= -21 \cdot 921 \; l. \text{ atmospheres.}$$

A_4 is numerically the same as A_2 but with $-$ *ve* sign.

$$\therefore \text{ The efficiency } = \frac{24 \cdot 605 - 21 \cdot 921}{24 \cdot 605}$$

$$= \frac{2 \cdot 684}{24 \cdot 605}$$

$$= 0 \cdot 10907.$$

It can also be calculated from temperatures.

$$\text{The efficiency } = \frac{T_1 - T_2}{T_1} = \frac{273 - 243 \cdot 2}{273}$$

$$= \frac{29 \cdot 8}{273}$$

$$= 0 \cdot 1091$$

Ans. 0·1091.

Problems for Solution

Problem 55. A column of gas of composition represented by $H_2 + 3O_2$ and of length 540 mms. was compressed adiabatically into a length of 40 mms. without ignition; into a length of 36 mms. with ignition resulting. The initial temperatures of the gases are 17·6°C. and 15°C. respectively. If γ is 1·4, calculate the temperatures between which the ignition temperature lies.

Ans. 550°C. and 578°C.

Problem 56. Calculate the change in temperature corresponding to a pressure difference of one atmosphere. (Joule Thomson effect) for carbon dioxide at 0°C.

$$a = 3 \cdot 61; \quad b = 0 \cdot 0428; \quad C_p = 8 \cdot 9.$$

Ans. 0·770°.

Problem 57. Calculate the change in temperature corresponding to a pressure difference of one atmosphere. (Joule Thomson effect) for hydrogen at 0°C.

$$a = 0{\cdot}19; \quad b = 0{\cdot}023; \quad C_p = 6{\cdot}8.$$

Ans. + 0·02. There is a slight heating effect.

Problem 58. Calculate the molecular heat of reduction of ethylene to ethane, given the following data :—

Molecular heat of combustion of hydrogen	64·49 g. Cals.
" " " " " ethane	369·00 " "
" " " " " ethylene	332·00 " "

Ans. + 27·49 Cals.

Problem 59. Calculate the heat of formation of formic acid from the following data :—

Heat of combustion of Carbon	(C, O_2)	= 96960 Cals.
" " " " Hydrogen	(H_2, O)	= 68360 "
" " " " formic acid	(CH_2O_2, O)	= 65900 "

Ans. + 99420 Cals.

Problem 60. Find the heat of formation of aldehyde (i) gaseous (ii) liquid, from the following data :—

$(2C_2H_4O, 5O_2)$ liquid	= 551 Cals.
$(2C_2H_4O, 5O_2)$ gaseous	= 564 Cals.
(CO_2)	= 97 Cals.
$(2H_2, O_2)$ to water	= 136·7 Cals.

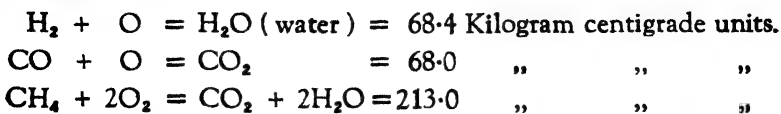
Ans. (i) + 48·7 Cals. (ii) + 55·2 Cals.

Problem 61. A gaseous hydrocarbon was analysed by explosion with the following result :—20 c. c. of hydrocarbon with 80 c. c. of oxygen gave 50 c. c. of residual gas, of which 40 c. c. were CO_2 and 10 c. c. O_2. When 2·86 litres of this hydrocarbon (measured over water at 13°C. and 751 mm.) were burnt in a Junker calorimeter, 2·6 litres of water were heated from an average temperature of 4° to an average temperature of 22°, and 5 c. c. of water were condensed from the products of combustion. Calculate the molecular heat of combustion (cals. evolved by

burning 22·4 litres) when the hydrogen of the hydrocarbon is burnt to steam and the carbon to carbon dioxide. Determine the hydrocarbon. Latent heat of steam 540 cals. Pressure of aqueous vapour at 13° = 11 mm.

Ans. C_2H_6; 371630 cals.

Problem 62. Calculate the gross calorific power of a cubic foot (at 0° and 760 mm.) of dry gas containing CO_2 = 13·2; CO = 15·3; H_2 = 19·5; CH_4 = 3·8; N = 48·2 per cent., assuming the following molecular heats of combustion :—

H_2 + O = H_2O (water) = 68·4 Kilogram centigrade units.
CO + O = CO_2 = 68·0 " " "
CH_4 + $2O_2$ = CO_2 + $2H_2O$ = 213·0 " " "

1 cubic foot of water = 28·3 litres. The gross calorific power includes the heat of condensation of the water. The net calorific power corresponds to the formation of water.

Ans. 40·2 Kg. cent. units.

Problem 63. Calculate the calorific intensity of carbon burning in oxygen and in air respectively if (CO_2) = 96960; specific heat of CO_2 = 0·2164; specific heat of N_2 = 0·2438 Composition of air = 79 volumes of nitrogen and 21 volumes of oxygen.

Ans. 10180°; 2755°.

Problem 64. On dissolving 100 grams of anhydrous copper sulphate in water, the heat evolved amounted to 9900 cals. whilst the same weight of crystallised copper sulphate ($CuSO_4$, $5H_2O$) gave an absorption of heat amounting to 1100 cals. Determine the heat of formation of the gram molecule of $CuSO_4$ into $CuSO_4$, $5H_2O$.

Ans. + 18535 cals.

Problem 65. Anhydrous magnesium chloride is to be prepared from magnesia, chlorine, and carbon. The heat of combustion of magnesium and oxygen, of magnesium and chlorine, and of carbon and oxygen are 145860, 151000, and

28600 cals. respectively in gram calories per gram molecule. Calculate the balance of gram calories given out or absorbed.

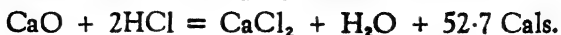
Ans. + 19440 cals.

Problem 66. From the following data calculate the thermal effect produced by the decomposition of ozone by hydrogen peroxide : —

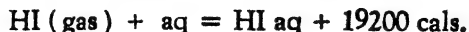
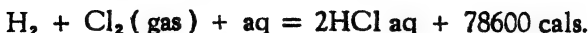
$$(H_2O) = 68000 \text{ cals.}$$
$$(H_2O_2) = 45000 \text{ cals.}$$
$$(O_2O) = -30000 \text{ cals.}$$

Ans. + 53000 cals.

Problem 67. Calculate the heat of combustion of calcium and oxygen from the following equations : —

$$CaO + 2HCl = CaCl_2 + H_2O + 52{\cdot}7 \text{ Cals.}$$
$$Ca + Cl_2 = CaCl_2 + 169{\cdot}8 \text{ Cals.}$$
$$H_2 + O = H_2O + 57{\cdot}9 \text{ Cals.}$$
$$H + Cl = HCl + 22{\cdot}0 \text{ Cals.}$$

Ans. + 131·0 Cals.

Problem 68. From the following data calculate the heats of formation of gaseous hydrochloric and hydriodic acids respectively

$$H_2 + Cl_2 \text{ (gas)} + aq = 2HCl\ aq + 78600 \text{ cals.}$$
$$HCl \text{ (gas)} + aq = HCl\ aq + 17300 \text{ cals.}$$
$$2HI\ aq + Cl_2 \text{ (gas)} = 2HCl\ aq + I_2 + 52400 \text{ cals.}$$
$$HI \text{ (gas)} + aq = HI\ aq + 19200 \text{ cals.}$$

Ans. [H, Cl] = + 22000 cals.; [H, I] = − 6100 cals.

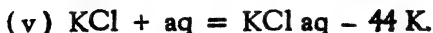
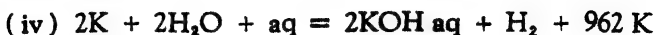
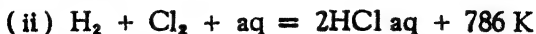
Problem 69. From the following data, calculate the heat of formation of solid potassium chloride from its elements :—

(i) $KOH\ aq + HCl\ aq = KCl\ aq + 137{\cdot}5\ K$

(ii) $H_2 + Cl_2 + aq = 2HCl\ aq + 786\ K$

(iii) $2H_2 + O_2 = 2H_2O + 136{\cdot}8\ K$

(iv) $2K + 2H_2O + aq = 2KOH\ aq + H_2 + 962\ K$

(v) $KCl + aq = KCl\ aq - 44\ K$

Ans. + 1055·5 K.

Problem 70. The heat of formation of hypochlorous acid has been determined by two independent methods by Thomsen; his results are given below. From both sets calculate the heat of formation of an aqueous solution of the acid (H, Cl, O, aq).

A		B	
($2NaOH$ aq Cl_2)	= 24647	($HOCl$ aq $2HI$ aq)	= 51435
($NaOH$ aq $HClO$ aq)	= 9976	(H, I aq)	= 13171
($NaOH$ aq HCl aq	= 13740		
(H, Cl aq)	= 39315		
(H_2, O)	= 68357.		

Ans. A 29973. B 29895.

Problem 71. In order to determine the heat of formation of ammonia, Thomsen passed chlorine into its aqueous solution and found for the reaction [$4NH_3$ aq 3Cl] an evolution of 119613 heat units; he also found for

[H, Cl] = 22001 ; [NH_3 aq HCl aq] = 12270

[HCl aq] = 17314 ; [NH_3 aq] = 8435.

But afterwards by the combustion of ammonia he found

[$2NH_3$3O] = 181296 ; [H_2 O] = 68357.

Calculate the heat of formation of ammonia from each set of data, and compare and contrast the reliability and probable sources of error in each method.

Ans. (1) + 26707 cals.; (2) + 11887 cals.

The second method is more direct than the first one, involves only two operations and is, therefore, less liable to error.

Problem 72. Calculate the heat of formation of water from the following data obtained by Than. Oxygen and hydrogen were exploded in a bomb in an ice calorimeter. For two grams of hydrogen, 838·6 grams of ice were melted. The latent heat of fusion of ice is 79·9 gram cals. Ostwald has shown that 970 gram cals. must be added, for correction. (H = 1·008).

Ans. 67510 gram cals.

68480 gram cals. after Ostwald's correction.

Problem 73. From the following data, two independent calculations of the heat of formation of iodic acid in aqueous solution may be made. Determine the mean value of this quantity :– (1) The reduction of one gram molecule of iodic acid by hydriodic acid to iodine in aqueous solution is accompanied by the evolution of 83·33 Cals. (2) The oxidation of one gram molecule of hydriodic acid to iodic acid by hypochlorous acid in aqueous solution is accompanied by a heat evolution of 70·68 Cals.

$$(H, I, Aq) = 13{\cdot}17 \text{ Cals.}; (H, Cl, Aq) = 39{\cdot}32 \text{ Cals.};$$
$$(H, Cl, O, Aq) = 29{\cdot}93 \text{ Cals.}; \quad (H_2, O) = 68{\cdot}35 \text{ Cals.}$$

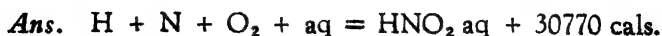
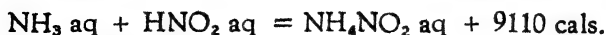
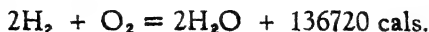
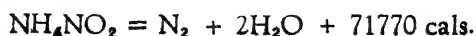
Given further that the heats of solution of iodic acid and iodine pentoxide are respectively = 2·17 Cals, and 1·79 Cals. Calculate the heats of formation of solid iodic acid and iodine pentoxide.

Ans. The heat of formation of iodic acid in aqueous solution by (1) is 55·68 Cals. and by (2) 55·90 Cals. The mean value is 55·79 Cals.

The heat of formation of solid iodic acid calculated from the mean value is 53·62 Cals. Similarly the heat of formation of iodine pentoxide is 51·83 Cals.

Problem 74. From the following data calculate the heat of formation of HNO_2 aq.

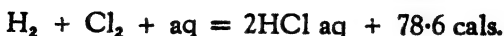
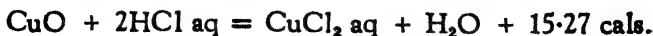
$$NH_4NO_2 = N_2 + 2H_2O + 71770 \text{ cals.}$$
$$2H_2 + O_2 = 2H_2O + 136720 \text{ cals.}$$
$$N_2 + 3H_2 + aq = 2NH_3\, aq + 40640 \text{ cals.}$$
$$NH_3\, aq + HNO_2\, aq = NH_4NO_2\, aq + 9110 \text{ cals.}$$
$$NH_4NO_2 + aq = NH_4NO_2\, aq - 4750 \text{ cals.}$$

Ans. $H + N + O_2 + aq = HNO_2\, aq + 30770$ cals.

Problem 75. From the thermo-chemical equations given, calculate the heat of formation of (1) CuO, and (2) $CuCl_2$ (anhydrous).

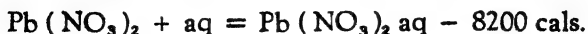
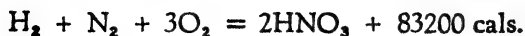
$$CuSO_4\, aq + Fe = FeSO_4 + Cu + 37{\cdot}4 \text{ cals.}$$
$$Fe + H_2SO_4\, aq = FeSO_4\, aq + H_2 + 24{\cdot}84 \text{ cals.}$$
$$H_2 + O = H_2O + 68{\cdot}36 \text{ cals.}$$

$$CuO + H_2SO_4\,aq = CuSO_4\,aq + H_2O + 18{\cdot}8 \text{ cals.}$$
$$CuO + 2HCl\,aq = CuCl_2\,aq + H_2O + 15{\cdot}27 \text{ cals.}$$
$$H_2 + Cl_2 + aq = 2HCl\,aq + 78{\cdot}6 \text{ cals.}$$
$$CuCl_2 + aq = CuCl_2\,aq + 11{\cdot}08 \text{ cals.}$$

(These are big calories).

Ans. (1) $Cu + O = CuO + 37$ cals.

(2) $Cu + Cl_2 = CuCl_2 + 51{\cdot}43$ cals.

Problem 76. From the following data calculate the heat of formation of $Pb(NO_3)_2$ from its elements :—

$$PbO + 2HNO_3\,aq = Pb(NO_3)_2\,aq + H_2O + 17000 \text{ cals.}$$
$$2Pb + O_2 = 2PbO + 101600 \text{ cals.}$$
$$H_2 + N_2 + 3O_2 = 2HNO_3 + 83200 \text{ cals.}$$
$$HNO_3 + aq = HNO_3\,aq + 7180 \text{ cals.}$$
$$2H_2 + O_2 = 2H_2O + 136000 \text{ cals.}$$
$$Pb(NO_3)_2 + aq = Pb(NO_3)_2\,aq - 8200 \text{ cals.}$$

Ans. 105560 cals. heat of formation.

Problem 77. The molecular heat of formation of liquid water from gaseous oxygen and hydrogen is + 68000 cals. When 10 grams of sodium react with large excess of water + 18800 cals. are set free and when 20 grams. of Na_2O react with a large excess of water + 20400 cals. are set free. From these data calculate the heat of formation of Na_2O.

Ans. 91240 cals.

Problem 78. A regenerative furnace holds 10 crucibles each containing 100 lbs. of steel. Assume (1) that the total heat in each lb. of steel when melted = 300 cals.; (2) that the furnace is fed by a gas with a calorific power of 480 cals. per cubic foot; (3) that only 5 per cent. of the heat generated is used for melting steel. Required the number of cubic feet of the gas for melting 1 ton (= 2000 lbs.) of steel.

Ans. 25000 cubic feet.

Problem 79. Calculate the temperature of hydrogen flame burning in (*a*) oxygen, and (*b*) dry air. Heat of combustion of 1 cubic metre of hydrogen is 2613 kilo. cals. The mean specific heat of water vapour between 0° and $t°$ = 0·34 + 0·00015t, and that of oxygen and nitrogen = 0·303 + 0·000027t.

Ans. 3660°; 1950°.

Problem 80. From the following data, based on the use of semi-normal solutions throughout, calculate the heat which should be liberated in the production, in aqueous solutions, of one gram molecule of ammonium acetate. 250 c.c. of caustic soda mixed with an equal volume of hydrochloric acid liberate 1710 calories; the same volume of caustic soda and acetic acid liberate 1620 cals. and of ammonia and hydrochloric acid 1530 cals. For the purpose of calculation, it is assumed that in the solution employed, the caustic soda and hydrochloric acid are fully dissociated.

Ans. 11520 cals.

Problem 81. According to Thomsen the mixture of 2NaOH aq with $2NHO_3$ aq evolves 27364 cals. 2NaOH aq + H_2SO_4 aq, 31378 cals. and $2NaNO_3$ aq and H_2SO_4 aq 576 cals. Calculate the thermal effect of mixing $2HNO_3$ aq with Na_2SO_4 aq (dilute solutions are used throughout).

Ans. 3438 cals. will be absorbed.

Problem 82. The specific volume of ice is 1·091 c. c. and that of water is 1·00 c. c., and the latent heat of fusion of ice is 79·8 cals. per gram. Calculate the lowering of the melting point of ice if the pressure is increased by one atmosphere. (1 gram cal. = 42670 gm. cm., and 1 atm. = 1033·3 gm. per sq. cm.).

Ans. 0·0076.

Problem 83. The transition point of rhombic sulphur into monoclinic sulphur under its own vapour pressure is 95·5°C. What will be its transition point under a pressure of one atmosphere? Latent heat of conversion per gram is 2·52 cals. Specific

volume of monoclinic (Vm) is greater than that of rhombic (Vr). $Vm - Vr = 0{\cdot}0126$ c. c. Calorie = 41·3 c. c. atmosphere.

Ans. 0·045°C. rise in transition point per atmosphere.

Problem 84. The vapour pressure of water at 99·8°C. is 754·58 mms. and at 100·2°C., it is 765·45 mms. Calculate the latent heat of vaporisation for 1 gram of water at 100°C. Regnault's value for 100° is 537 cals. How do you account for the difference between the calculated and experimental values?

Ans. 551·6 cals./g. The difference is due to the assumption that steam behaves like a perfect gas.

Problem 85. At what height must the barometer stand in order that water may boil at 101°C?

$$ln = \log \times 2{\cdot}303; \quad L = 536 \text{ cals per g.}$$

Ans. 785·7 mm.

Problem 86. The vapour pressure of an organic liquid at 20°C. and 40°C. are 74·6 mm. and 181·8 mm. respectively. The gas constant R = 2 calories (approx.) and $\log_e x = 2{\cdot}303 \log_{10} x$. Calculate the latent heat of vaporisation of the liquid.

Ans. 8168 cals. per gram mol.

CHAPTER III

SOLUTIONS

16. **Relation between the lowering of vapour pressure in a solution and its concentration :**

Raoult's Law :—

$$\frac{P_1 - P_0}{P_1} = \frac{n}{N + n} \approx \frac{n}{N} \text{ (when the solution is dilute),}$$

where P_1 = vapour pressure of the solvent ;
P_0 = vapour pressure of the solution ;
n = mols of solute ; and
N = mols of solvent.

The relation can be derived by the following cyclic operation :—

(i) Remove $\frac{N}{n}$ molecules of the solvent (which contain one mol of the solute) from the solution osmotically.*

Work is done on the solution and it is $-$ RT. It is assumed that the total volume of the solution is so great that the removal of $\frac{N}{n}$ molecules of the solvent will not appreciably alter its concentration.

(ii) Vaporise the removed solvent at P_1, then the work done is

$$\frac{N}{n} P_1 V_1.$$

(iii) Lower the pressure from P_1 to P_0 isothermally and reversibly, then the work done is

$$RT \log \frac{P_1}{P_0} \cdot \frac{N}{n} .$$

* This could be done reversibly by employing a pressure slightly more than the osmotic pressure of the solution, the solvent being forced out from the solution through the walls permeable to the solvent.

(iv) The vapour at P_0 is allowed to mix with the solution at P_0, then the work done in the condensation is,

$$\frac{N}{n} P_0V_0 \text{ and the cycle is complete.}$$

Works done in (ii) in evaporation and in (iv) in the condensation are equal,

$$\therefore \quad RT \log \frac{P_1}{P_0} \cdot \frac{N}{n} - RT = 0$$

$$\text{or} \quad RT \log \frac{P_1}{P_0} \cdot \frac{N}{n} = RT$$

$$\text{But } RT \log \frac{P_1}{P_0} = - RT \log \frac{P_0}{P_1} = - RT \log \left(1 - \frac{P_1 - P_0}{P_1}\right)$$

Note :– $\log (1 - x) = - x + x^2 - x^3$............and if x is small, higher powers of x can be neglected and $\log (1 - x) \approx - x$.

Since $\frac{P_1 - P_0}{P_1}$ is small,

$$- RT \log \left(1 - \frac{P_1 - P_0}{P_1}\right) \approx RT \frac{P_1 - P_0}{P_1}$$

$$\therefore \quad RT \frac{P_1 - P_0}{P_1} \cdot \frac{N}{n} \approx RT$$

$$\therefore \quad \frac{P_1 - P_0}{P_1} \cdot \frac{N}{n} \approx 1$$

$$\therefore \quad \frac{P_1 - P_0}{P_1} \approx \frac{n}{N}.$$

Extending the gas laws to solution :—

$\underline{P}V = nRT$, ($\underline{P}$ is the osmotic pressure of the solution).

$$\therefore \quad \underline{P} = \frac{nRT}{V}.$$

If S_1 is the density of solution,

$$V = \frac{Nm}{S_1}, \quad (m = \text{molecular weight of solvent}).$$

$$\underline{P} = \frac{nRT}{1} \times \frac{S_1}{Nm} = \frac{n}{N} \cdot \frac{S_1RT}{m} = \frac{nSRT}{Nm}.$$

(In a dilute solution $S_1 \approx S$ the density of solvent.)

Thus, $\underline{P}$, $\frac{n}{N}$ and $\frac{P_1 - P_0}{P_1}$ could be determined if one of the magnitudes is known.

If S is the density of the solvent (c. c. being the unit), the value of $\underline{P}$ in atmospheres, when R is taken as being equal to 82·04 c. c. atmospheres, will be:

$$\underline{P} = \frac{S \times 82{\cdot}04 \times T}{m} \times \frac{P_1 - P_0}{P_1}.$$

If a litre (1,000 c. c.) is used as the unit, R = 0·08204 litre atmos. and

$$\underline{P} = \frac{1{,}000\ S \times 0{\cdot}08204 \times T}{m} \times \frac{P_1 - P_0}{P_1}$$

17. **Relation between the depression of the freezing point of a solution, its concentration, and the latent heat of fusion of the solvent.**

It is determined by the following cyclic process :—

T, freezing point of the solvent;

$T - dt$, freezing point of the solution;

n, number of mols of solute present in N mols of solvent, whose molecular weight is m;

H, the latent heat of fusion of one gram of the solvent.

I. $\frac{N}{n}$ mols of solvent (which contain one mol of solute) are frozen out from the solution at $T - dt$.

It is assumed that the solution is present in such large amounts that removal of $\frac{N}{n}$ mols of solvent would not appreciably alter its concentration.

Heat $q = \mathrm{H} \cdot \frac{m \cdot \mathrm{N}}{n}$ calories which are evolved at a temperature $\mathrm{T} - dt$.

II*a*. Both the solid and the solution are warmed from $\mathrm{T} - dt$ to T.

II*b*. The solid solvent $\frac{\mathrm{N}}{n}$ is fused at T.

Heat $q = \mathrm{H} \cdot \frac{m \cdot \mathrm{N}}{n}$ which is absorbed at the temperature T.

III. The solvent is reversibly and osmotically mixed with the solution. Work done by the system = RT.

IV. The solution is cooled from T to $\mathrm{T} - dt$ to restore the original condition.

Operations II*a* and IV approximately cancel each other. In II*b*, heat q is absorbed at a temperature T, and heat q is evolved in I at a temperature $\mathrm{T} - dt$, and $d\mathrm{A}$ is work done which $= q . \frac{dt}{\mathrm{T}}$, and RT is the work done in III.

$$\text{Thus} \quad q \frac{dt}{\mathrm{T}} = \mathrm{RT}.$$

$$\therefore \quad dt = \frac{\mathrm{RT}^2}{q} = \mathrm{RT}^2 \div \mathrm{H} \frac{m\mathrm{N}}{n} = \frac{\mathrm{RT}^2 \cdot n}{\mathrm{H} \cdot m\mathrm{N}}$$

$$= \frac{\mathrm{RT}^2}{\mathrm{H}} \cdot \frac{n}{\mathrm{W}}$$

(mN, the weight of the solvent which contains 'n' solute is called W.)

If one mol is dissolved in 100 grams of solvent,

$$dt = \frac{\mathrm{RT}^2}{\mathrm{H}} \cdot \frac{1}{100}$$

$$\approx \frac{0{\cdot}02\mathrm{T}^2}{\mathrm{H}} \qquad \because \quad (\mathrm{R} \approx 2 \text{ cals.})$$

18. Relation between the elevation of the boiling point of a solution, its concentration, and its latent heat of evaporation.

It is determined by the following cyclic process :—

T, the boiling point of the solvent;

T + dt, the boiling point of the solution;

n, the number of mols of solute present in N mols of solvent whose molecular weight is m;

H, the latent heat of evaporation of one gram of the solvent;

I. $\frac{N}{n}$ mols of solvent which contain one mol of solute are removed from the solution at T + dt reversibly by evaporation. Heat $q = H \cdot \frac{mN}{n}$ is absorbed at T + dt. It is assumed that the solution is present in such large amount that removal of $\frac{mN}{n}$ mols of solvent from the solution by evaporation would not appreciably alter its concentration.

II a. Both the vapour and the solution are cooled from T + dt to T.

II b. The vapour is condensed at T. Heat $q = H \cdot \frac{mN}{n}$ is evolved at the temperature T.

III. The condensed solvent is reversibly and osmotically mixed with the solution; work done by the system = RT.

IV. The solution is warmed from T to T + dt to restore the original condition.

Operations II a and IV approximately cancel each other.

In I, heat q is absorbed at T + dt, and in II b heat q is evolved at T, and dA, the work obtained $= q\frac{dt}{T}$; and RT is the work done in III.

$$q \frac{dt}{T} = RT.$$

$$\therefore \quad dt = \frac{RT^2}{q} = RT^2 \div H \cdot \frac{mN}{n} = \frac{RT^2 \cdot n}{H \cdot mN}$$

$$= \frac{RT^2}{H} \cdot \frac{n}{W}$$

(mN, the weight of the solvent containing n mols of solute is called W).

∴ If one mol is dissolved in 100 grams of the solvent ($n = 1$ and $W = 100$), then

$$dt = \frac{RT^2}{H} \cdot \frac{1}{100} \approx \frac{0{\cdot}02\,T^2}{H} \quad \because \quad (R \approx 2 \text{ cals.})$$

19. Relation between $\underline{P}$, the relative lowering of the vapour pressure $\frac{P_1 - P_0}{P_1}$, the concentration $\frac{n}{N}$, the lowering in the freezing point and the elevation of the boiling point, are summarised below :

$$dt = \frac{RT^2}{H} \cdot \frac{n}{mN} = \frac{RT^2}{Hm} \cdot \frac{n}{N}$$

$$= \frac{RT^2}{m \cdot H} \cdot \frac{P_1 - P_0}{P_1}$$

$$= \frac{RT^2}{mH} \cdot \underline{P} \cdot \frac{m}{SRT}$$

$$= \frac{T}{mH} \cdot \underline{P} \cdot \frac{m}{S}$$

$$\text{or} \quad \underline{P} = \frac{dt}{T} \cdot H \cdot S$$

N. B.— Relation between calorie and c. c. atmosphere :—

1 cal. = 41·33 c. c. atmosphere

1 c. c. atmosphere = 0·02423 cal.

Problems with Solutions

Problem 87. The vapour pressure of a 2·1% of aqueous solution of a non-electrolyte at 100°C. is 755 mm. Calculate the molecular weight of the solute.

Solution : $\frac{P - P_1}{P} = \frac{n}{N}$ where $\frac{P - P_1}{P}$ is the relative lowering of vapour pressure and n and N are the molecules of the solute and solvent respectively in the solution.

$$\frac{760 - 755}{760} = \frac{2 \cdot 1 \times 18}{M \times 100}$$

$$M = \frac{2 \cdot 1 \times 18 \times 760}{100 \times 5}$$

$$= 57 \cdot 46$$

Ans. The molecular weight of the solute is 57·46.

Problem 88. The vapour pressure of water at 98°C. is 707·3 mm. What is the latent heat of evaporation ?

Solution : Use Clausius formula which gives the relation between vapour pressure and temperature. Assuming that vapour of water at 100°C. is 760 mm.,

$$\log \frac{P_1}{P_0} = \frac{-L}{2 \cdot 3R} \left(\frac{T_1 - T_0}{T_1 T_0} \right)$$

$$-L = \frac{T_1 T_0}{T_1 - T_0} \times 2 \cdot 3R \times \log \frac{P_1}{P_0}$$

$$i.e. \quad L = \frac{1 \cdot 985 \times 2 \cdot 3 \times 371 \times 373}{-2} \log \frac{707 \cdot 3}{760}$$

$$= -\frac{1 \cdot 985 \times 2 \cdot 3 \times 371 \times 373 \times 0 \cdot 03121}{2}$$

$$= -\frac{19712}{2}$$

$$= -9856 \text{ cals. per gram mol.}$$

Ans. The latent heat of evaporation of water is − 9856 cals. per gram mol.

Problem 89. The osmotic pressure of a solution of 0·184 g of urea in 100 c. c. of water is 56 cms. of mercury at 30°C. Calculate the molecular weight of urea.

Solution: Using the formula $\pi v = nRT$,

where π = osmotic pressure in atmospheres and

n = number of urea molecules in one litre,

$$\frac{56}{76} \times 0{\cdot}1 = \frac{0{\cdot}184}{M} \times 0{\cdot}08204 \times 303.$$

$$\therefore \quad M = \frac{0{\cdot}184 \times 0{\cdot}08204 \times 303 \times 76}{56 \times 0{\cdot}1}$$

$$= 62{\cdot}07.$$

Ans. The molecular weight of urea is 62·07.

Theoretical molecular weight of urea $OC\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix}$ is 60.

Problem 90. The osmotic pressure of a solution containing 3·42 grams of NaCl in 100 c. c. of water is 2268 cm . at 60°. Calculate the percentage dissociation of the salt.

Solution: The apparent molecular weight of NaCl is first calculated with the help of the following equation, $\pi v = nRT$.

If M' = apparent molecular weight of NaCl.

$$\text{then} \quad \frac{2268 \times 0{\cdot}1}{76} = \frac{3{\cdot}42}{M'} \times 0{\cdot}08204 \times 333.$$

$$\therefore \quad M' = \frac{3{\cdot}42 \times 0{\cdot}08204 \times 333 \times 76}{2268 \times 0{\cdot}1}$$

$$= 31{\cdot}30.$$

If a is the degree of dissociation,

$M'(1 + a) = M$, where M = the true molecular wt.

$$\therefore \quad 1 + a = \frac{58{\cdot}5}{31{\cdot}30}$$

$$\therefore \quad a = \frac{58{\cdot}5 - 31{\cdot}3}{31{\cdot}3}$$

$$= \frac{27\cdot2}{31\cdot3}$$

$$= 0\cdot8670 \text{ or } 86\cdot70\%.$$

Ans. 86·70%.

Problem 91. When 0·3 g of a substance (mol. wt. 150) is dissolved in 42 g of a certain solvent, the freezing point of the latter is lowered by 0·233°C. When 0·27 g of another substance is dissolved in 56 g of the same solvent, the observed depression of the F. P. is 0·218°C. Calculate the molecular weight of the second solute.

Solution : Find K from the data of the first solute, and use it to calculate the molecular weight of the second solute.

$$K = \frac{\Delta Mb}{100\,a}$$

$$= \frac{0\cdot233 \times 150 \times 42}{100 \times 0\cdot3}$$

$$= 48\cdot93.$$

If the molecular weight of the second solute is M',

$$\text{then } M' = \frac{100\,aK}{\Delta b}$$

$$= \frac{100 \times 0\cdot27 \times 48\cdot93}{0\cdot218 \times 56}$$

$$= 108\cdot22$$

Ans. The molecular weight of the second solute is 108·22.

Problem 92. A solution of 0·025 g of sodium in 100 g of mercury lowered the F. P. of mercury by 0·45°C. Given that the molecular depression of the F. P. of mercury is 425°C. per 100 g, calculate the molecular weight of sodium in the solution.

Solution : $M = \frac{K\,100\,a}{\Delta b}$

$$= \frac{425 \times 100 \times 0\cdot025}{100 \times 0\cdot45}$$

$$= 23\cdot61.$$

Ans. The molecular weight of sodium in mercury is 23·61.

Problem 93. 0·1315 g of camphor ($C_{10}H_{16}O$) dissolved in 5 g of *p*-toluidine (M. P. 42·1°) depresses the F. P. by 0·940°. Calculate the freezing point constant, and the latent heat of fusion per gram of *p*-toluidine.

Solution : $K = \frac{\Delta Mb}{100\,a}$, (the freezing point constant).

The molecular weight of camphor is (152).

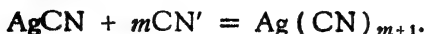
$$\therefore \quad K = \frac{152 \times 5 \times 0{\cdot}940}{100 \times 0{\cdot}1315}$$

$$= 54{\cdot}33, \text{ the freezing point constant.}$$

$$\text{The latent heat of fusion} = \frac{0{\cdot}02 \times (315{\cdot}1)^2}{54{\cdot}33} = 36{\cdot}55$$

Ans. 54·33 F. P. constant ; 36·55 cals. per gram.

Problem 94. The F. P. of 0·25N KCN solution is − 0·860°, and that of the same solution containing 0·25 gram mol of AgCN per litre is − 0·830°. The solution of AgCN in KCN takes place as,

$$AgCN + mCN' = Ag(CN)_{m+1}.$$

Calculate the value of *m* to the nearest whole number, given K = 1·86.

Solution : 0·25 mol of AgCN has been dissolved by combining with CN′ ions supplied by KCN which progressively dissociates it more and more as CN′ are removed as (AgCN) $_{m+1}$. The dissolved AgCN should produce an increase in the lowering of F. P. by 1·86 × 0·25 = 0·465.

If CN′ from KCN had not been removed to form the complex ion, the total lowering should have been (0·860 + 0·465) = 1·325. The actual lowering, however, is 0·83. The difference in the lowering is (1·325 − 0·83 =) 0·495. If one gram mol of CN′ has to be removed, the difference would have been 1·86. Therefore, the number of CN′ removed for the given difference

$$= \frac{0{\cdot}495}{1{\cdot}86} = 0{\cdot}2664.$$

These ions are removed by 0·25 gram mol of AgCN. Therefore, 1 mol of AgCN will remove,

$$\frac{0\cdot2664}{0\cdot25} = 1\cdot064.$$

Ans. $m = 1$ (approximately).

N. B.— The degree of dissociation (0·85) of KCN need not be taken into consideration, as is sometimes done in solving the problem. Since as CN′ ions are taken up by AgCN to form the complex ion $Ag(CN)_{m+n}$, progressive ionisation of KCN occurs till it gets completely dissociated.

Problem 95. A solution containing 0·5 g of a substance of molecular weight 182 dissolved in 42 g of C_6H_6 boils at 80·175°C. The B. P. of C_6H_6 is 80°C. What is the latent heat of evaporation ?

Solution : First find the constant K, and then with the help of this value, calculate the latent heat.

$$\Delta = \frac{K100\,a}{Mb}$$

where, Δ = elevation of B. P.
M = mol. wt. of the substance
b = wt. of solvent
a = wt. of the substance dissolved.

$$\therefore \quad K = \frac{\Delta Mb}{100\,a} = \frac{0\cdot175 \times 182 \times 42}{100 \times 0\cdot5} = 26\cdot754$$

$$\text{The latent heat } H = \frac{RT^2}{100\,K} = \frac{1\cdot985 \times (353)^2}{100 \times 26\cdot754}$$

$$= 92\cdot45.$$

Ans. 92·45 cals. per gram.

Problem 96. A solution containing 0·4344 g of anthracene in 44·16 g of acetic acid (B. P. 118·1°) boils at 118·240°C. Calculate the molecular weight of anthracene, given that the latent heat of evaporation of acetic acid per gram is 121 calories.

Solution : First find the value of K;

$$K = \frac{RT^2}{1000\,l}$$

$$= \frac{1.985 \times (391.1)^2}{1000 \times 121}$$

$$= 2.509$$

Now use this value of K to find the value of M

$$M = \frac{K \times 1000 \times a}{\Delta \times b}$$

$$= \frac{2.509 \times 1000 \times 0.4344}{0.140 \times 44.16}$$

$$= 176.4.$$

Ans. The molecular weight of anthracene is 176·4. Theoretical molecular weight of authracene ($C_{14}H_{10}$) is 178.

Problem 97. An aqueous solution of $Ba(NO_3)_2$ containing 120·1 g / litre boils at 100·4°C. Calculate the degree of dissociation of the salt. (l for water = 536 cals.)

Solution : Calculate the constant K from the given latent heat for water. Using this value, find the apparent molecular weight of $Ba(NO_3)_2$ from which the degree of dissociation can be readily found out.

$$K = \frac{RT^2}{1000\, l}$$

$$= \frac{1.985\,(373)^2}{1000 \times 536}$$

$$= 0.5164.$$

The apparent molecular weight (M^1) of $Ba(NO_3)_2$ is

$$M^1 = \frac{K\, 1000\, a}{\Delta\, b}, \text{ where}$$

a = substance dissolved,
b = weight of the solvent,
Δ = elevation of B. P.

$$= 124.3.$$

M of $Ba(NO_3)_2$ is (137·4 + 28 + 96) = 261·4.

If α is the degree of dissociation, then,

$$M^1(1 + 2\alpha) = M.$$

$$\therefore \quad 124{\cdot}3\,(1 + 2\alpha) = 261{\cdot}4.$$

$$\therefore \quad 2\alpha = \frac{261{\cdot}4}{124{\cdot}3} - 1$$

$$= \frac{137{\cdot}1}{124{\cdot}3}$$

$$= \frac{137{\cdot}1}{124{\cdot}3}$$

$$= 1{\cdot}104$$

or, $\alpha = 0{\cdot}552.$

Ans. The degree of dissociation is 0·552.

Problems for Solution

Problem 98. The vapour pressure of a solution containing 8·89 grams of dextrose in 100 grams of water is 4·582 mm. at 0°C. and that of pure water at the same temperature is 4·620 mm. Calculate the molecular weight of dextrose.

Ans. 194·55 molecular wt. The theoretical molecular wt. of dextrose ($C_6H_{12}O_6$, H_2O) is 198.

Problem 99. The vapour pressure of benzene at 20°C. is 75·0 mm. and at 30°C., 118·0 mm. of mercury. Calculate the molecular heat of vaporisation of benzene.

Ans. – 7978 cals. per gram mol.

Problem 100. A current of dried air was passed through a solution of 3·458 grams of a substance in 100 grams of ethyl alcohol, and then passed through ethyl alcohol alone. The loss in weight of the solution was 0·9420 gram and that of the ethyl alcohol, 0·9675 gram. Find the molecular weight of the dissolved substance.

Ans. 61·2.

Problem 101. The vapour pressure lowering of alcoholic solutions gave the following results by the dynamic method :—

Substance	Wt. dissolved in 50 grams alcohol	b_1	b_2
Nitrobenzene	4·1	2·034	0·0684.
Benzoic acid	4·28	1·8315	0·0731.
Acetamide	5·04	0·6073	0·0525.
Atropine	5·05	1·467	0·027.
Vanillin	2·4	1·6895	0·0312.

b_1 = loss in weight of the solution,

b_2 = loss in weight of alcohol.

Calculate the molecular weight of these substances from the above data.

Ans. Nitrobenzene = 112·1 ; Benzoic acid = 98·6 ;
Acetamide = 53·6 ; Atropine = 252 ;
Vanillin = 119·5.

Problem 102. Raoult found that a solution of 11·346 grams of turpentine in 100 grams of ether $(C_2H_5)_2O$ had a vapour pressure of 360·1 mm. At the temperature of the experiment, the vapour pressure of pure ether was 383. Calculate the molecular weight of turpentine.

Ans. 132·2.

Problem 103. Berkley and Hartley found the following results in experiments on the lowering of the vapour pressure of sugar solutions by the dynamic method :—

conc. of Sugar solution, g per litre	density of solution, g / c. c.	loss in weight	
		solution	water
285	1·119	1·8054	0·0380
420	1·187	1·2882	0·0394

Calculate the molecular weight of the sugar.

Ans. 292·2 ; 322·2.

Problem 104. Frazer, Lovelace and Rogers found that 17·930 grams of mannitol dissolved in 1900 grams of water lowered the vapour pressure of water at the temperature of the experiment by 17·19 mm. Calculate the molecular weight of mannitol.

Ans. 180·5.

Problem 105. An amalgam containing 1·142 g of tin dissolved in 100 g of mercury, was heated in the vapour of mercury boiling at a pressure of 768·8 mm. The vapour pressure over the amalgam was 754·1 mm. What is the molecular weight of tin.

Ans. 119·8.

Problem 106. De Vries found that a 3·42% solution of cane sugar was isotonic with 5·96% solution of raffinose, molecular weight of cane sugar being 342. Calculate the molecular weight of raffinose.

Ans. 596.

Problem 107. A $\frac{N}{10}$ solution of $NaC_2H_3O_2$ is ionised to the extent of 80% at 18°C. What is the osmotic pressure of the solution at this temperature.

Ans. 4·253 atmospheres.

Problem 108. A solution of urea in water at 50°C. has a vapour pressure of 90·62 mm. Water at the same temperature has a vapour pressure of 92 mm. Calculate the osmotic pressure of the solution.

Ans. 22·15 atmospheres.

Problem 109. Vapour pressure of a sucrose solution containing 3·42 grams of sucrose in 100 grams of water is 4·517 mm. at 0°C. Vapour pressure of water at 0° is 4·6 mm. Find the osmotic pressure of the solution.

Ans. 22·5 atmospheres.

Problem 110. A 1·46% solution of cane sugar has an osmotic pressure of 783 mm. at 30°. What is the molecular weight of cane sugar ?

Ans. Molecular wt. of cane sugar is 352·2. (Theoretical molecular wt. of cane sugar ($C_{12}H_{22}O_{11}$) is 342.)

Problem 111. 3·29 grams of a substance dissolved in 100 grams of water (K = 18·5) gave a depression of the freezing point of 2·04°C. Find the molecular weight of the substance.

Ans. 30·4.

Problem 112. Successive quantities of 0·317, 0·394 and 0·5152 gram of a substance were dissolved in 18·054 grams of benzene. The depression of freezing point were 0·278°, 0·348°, and 0·452° respectively. What was the molecular weight of the substance ? The molecular lowering of the freezing point of benzene in 100 c. c. is 50°.

Ans. 315.

Problem 113. The addition of 0·1407 g of mesitylene (C_9H_{12}) to 11·375 g of palmitic acid ($C_{16}H_{32}O_2$) lowered the F. P. of the latter from 62·25°C. to 61·81°C. Find the latent heat of fusion per gram of palmitic acid.

Ans. 52·61 cals./g.

Problem 114. Beckmann determined the molecular weight of selenium tetrachloride ($SeCl_4$) by the F. P. method, using solutions of the substance in glacial acetic acid. The following results were obtained :—

Weight of acetic acid gm.	Weight of $SeCl_4$ gm.	F. P. lowering °C.
20·3	0·1337	0·180
20·3	0·2209	0·295
20·3	0·3112	0·409

The depression constant for acetic acid (for 100 g) is 39°C. Calculate the molecular weights.

Ans. 142·8 : 143·8 ; 146·2. (Theoretical = 221.)

Problem 115. The freezing point of naphthalene is 80°C. On adding to 10 grams of naphthalene, 2 grams of a certain substance, the observed freezing point was 78·6°C. The latent heat of fusion of naphthalene is 35·5 cals. per g. Calculate the molecular weight of the added substance.

Ans. Molecular wt. of the added substance is 995·6.

Problem 116. The melting point of phenol is 40°C. A solution containing 0·344 g of acetamide in 25·08 g of phenol freezes at 39·45°C. Assuming that acetamide has normal molecular weight in phenol, calculate the freezing point constant, and latent heat of fusion of phenol ? (The molecular weight of acetamide = 135).

Ans. K = 54·13 (53 given in text books).
34·92 cals. per gram.

Problem 117. 100 grams of water dissolve 3 and 5·33 grams of a solid acid at 0°C. and 10°C. Find the molecular heat of solution of the acid.

Ans. – 8162 cals.

Problem 118. 2·447 gram of chloral hydrate dissolved in 100 grams of acetic acid lowered its freezing point by 0·755°. Assuming K = 39 in the case of acetic acid, calculate the degree of dissociation of the chloral hydrate.

Ans. 0·31.

Problem 119. Calculate the osmotic pressure of an aqueous solution containing 5·0 grams of a dissolved substance per litre at the freezing point of the solution, given that the solution freezes at – 0·25°C. The molecular lowering of the freezing point may be taken at 18·5.

Ans. 3·02 atmospheres.

Problem 120. Calculate the latent heat of fusion of tin from the following data : melting point of tin = 232°C. The depression of the freezing point of 1 gram atom of silver per 100 gram atom is 3·0°C.

Ans. 1688 calories per gram atom.

Problem 121. A solution contains 85·5 g of sucrose in 1000 g of water and is also $\frac{N}{100}$ with respect to HCl. Calculate as nearly as possible the F. P. of (i) the freshly prepared solution; and of (ii) the solution after half of the sucrose has been inverted. Molecular depression for 1 kg of water = 1·855.

Ans. − 0·5008°; − 0·7326°.

Problem 122. A solution containing 0·001 g molecules of $ZnCl_2$ in 1000 g of water freezes at − 0·0055°C. while one containing 0·081 g mols freezes at − 0·3854°C. If the constant for water is 1·85 per 1000 g, calculate the degree of dissociation of $ZnCl_2$.

Ans. 0·9865; 0·7705.

Problem 123. An element exists in two allotropic forms α and β. The α form is insoluble in carbon disulphide. A pure sample of the β form initially melted at 119·25°C. but in the course of a few minutes the melting point fell to 114·5°C. When the element had completely melted at this temperature, the liquid was plunged into ice cold water, and 3·6% of the resultant solid was then found to be insoluble in carbon disulphide. Deduce the molecular weight of the α form. The latent heat of fusion of the β form is 9 cals. per gram.

Ans. Molecular weight of the α form is 183·9.

Problem 124. The freezing point of a solution of barium hydroxide containing one gram molecule of the salt in 60 litres is − 0·0888°C. Calculate the degree of dissociation of the salt, and the pH of the solution, given K = 1·89 for concentrations in gram molecules per litre, and the ionisation constant for water = $1{\cdot}2 \times 10^{-14}$.

Ans. Degree of dissociation, 0·9095; pH = 12·4024.

Problem 125. A solution of 0·684 gram of cane sugar in 100 grams of water has the freezing point − 0·037°. A solution of 0·585 gram NaCl in 100 grams of water freezes at − 0·342°.

Calculate the apparent molecular weight of NaCl and its degree of dissociation.

Ans. Apparent molecular weight, 31·65.
Degree of dissociation, 0·848.

Problem 126. 2·012 grams of resorcinol are dissolved in 100 grams of ether. The rise in the B. P. is 0·399°. Find the molecular weight of resorcinol, being given that the B. P. of ether is 34·8°, and the latent heat of vaporisation is 84·5 calories.

Ans. 112·1.

Problem 127. A solution containing 0·5 g of a substance of molecular weight 182 dissolved in 42 grams of benzene boils at 80·175°. The boiling point of benzene is 80·000°C. What is the latent heat of evaporation ?

Ans. 93·17 cals./g.

Problem 128. Beckmann determined the molecular weight of sulphur in bromine by the elevation of the boiling point with the following results :—

Wt. of Bromine g	Wt. of Sulphur g	Elevation °C.
42·0	0·0666	0·132
42·0	0·1076	0·903
42·0	0·1745	0·319
42·0	0·2863	0·511

The elevation constant of bromine for 100 g is 52. Calculate the molecular weights of sulphur.

Ans. 62·47 ; 65·6 ; 67·74 ; 69·39.

Problem 129. The boiling point of pure acetone is 56·38°C. at normal barometric pressure. A solution of 0·707 g of a compound in 10 g of acetone boiled at 56·88°C. What is the molecular weight of the compound if the molecular elevation constant for acetone per 100 g is 16·7 ?

Ans. 236.

Problem 130. 0·4559 g of iodine dissolved in 30·14 g of ether raised the boiling point from 35°C. to 35·126°C. The molecular weight of ether is 74, and the latent heat of evaporation is 90 cals. per gram. Find the molecular weight of iodine.

Ans. 253·1.

Problem 131. The following values of the elevation of the boiling point were obtained when naphthalene ($C_{10}H_8$) was dissolved in chloroform ;—

Naphthalene	1·0171	2·0266	5·0695	7·0898 grams
Elevation	0·475°	0·942	2·320°	3·205°C.

60·81 grams of chloroform were used throughout. The boiling point of chloroform is 61·2°C. and the latent heat of vaporisation of one gram of chloroform is 61 cals. Calculate the molecular elevation for 100 grams of the solvent both from the latent heat of vaporisation, and from the elevation of the boiling point.

Ans. 36·35 from the latent heat:
35·25 from the elevation of the boiling point.

Problem 132. Calculate the molecular weight of a substance from the following data :—

Weight of the substance	0·260 gram.
Weight of the solvent	10·8 grams.
Rise of B. P.	0·400°C.
B. P. of pure solvent	80·2°C.
Heat of vaporisation of solvent	93·4 gram calories.

Ans. 160·8.

Problem 133. The solution of 1·065 grams of a substance in 30·14 grams of ether produced a rise of 0·296° in the B. P. The constant of ether is 21·1. Find the molecular weight of the substance and explain fully the principle involved.

Ans. 251·9 molecular weight. For the principle involved *vide* p. 65.

Problem 134. 50 grams of pure CS_2 were placed in a boiling point apparatus. The B. P. was found to be 46·3°C. Benzoic acid was added and the following results were obtained.

Benzoic acid added	Elevation of the B. P.
1·6430 grams	0·320°
4·5520 grams	0·790°.

Latent heat of vaporisation of CS_2 is 85·3 cals. per gram. What conclusions do you draw as to the state of benzoic acid in the solution.

Ans. Benzoic acid is associated and the degree of association varies directly with concentration. Molecular Wts. 245·5 and 275·4.

Problem 135. Under a pressure of 760 mm. ether boils at 35°C. A solution of 10·44 g of aniline in 100 grams of ether has a vapour pressure of 333 mm. at 15·3°C. The latent heat of evaporation of ether is − 89·73 cals. per gram. Calculate the molecular weight of aniline in the solution.

Ans. Mol. Wt. 89·32. (Theoretical Mol. Wt. = 93).

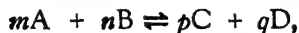
Problem 136. The boiling point of a solution containing 3·40 grams of anhydrous $BaCl_2$ in 100 grams of water is 100·208°C. Calculate the degree of dissociation of $BaCl_2$. K for 1000 grams of the solvent is 0·52 (Ba = 137·4 ; Cl = 35·46).

Ans. The degree of dissociation is 0·725.

CHAPTER IV

MASS ACTION

20. The Law of Mass Action.— In the reaction

$$mA + nB \rightleftharpoons pC + qD,$$

at a temperature T, when it reaches equilibrium, the following relation is valid and is called the law of mass action :

$$\frac{Pc^p \times Pd^q}{Pa^m \times Pb^n} = K.$$

A, and B are the substances which react, C and D are the products formed, P*a*, P*b*, P*c* and P*d* are their respective partial pressures at ***equilibrium***, *m*, *n*, *p* and *q* are the number of mols of the respective reacting substances and products formed and K the constant.

Van't Hoff assumed the reaction to occur in equilibrium boxes, kept at different pressures, and by carrying out the reaction in a cyclic way, he obtained a rigid proof of the Law of Mass Action.

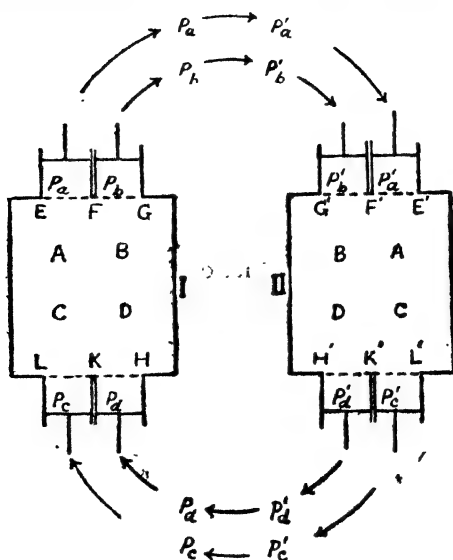



Fig. 4. Equilibrium Boxes

I and II are two equilibrium boxes; I contains A, B, C and D at the equilibrium partial pressures Pa, Pb, Pc and Pd at the temperature T and, II contains A, B, C and D at the equilibrium partial pressures $P'a$, $P'b$, $P'c$ and $P'd$ also at the temperature T. Portion of the wall EF in I and E'F' in II is permeable to A; FG and F'G' to B; LK and L'K' to C; and HK and H'K' to D.

I. Remove* reversibly through the wall permeable to A m mols of A at the pressure Pa; work done being mRT.

Ia. Change the pressure from Pa to $P'a$ isothermally and reversibly. W_1, the work done is $mRT \log \frac{Pa}{P'a}$.

Ib. Introduce m mols of A at the pressure $P'a$ into II reversibly; work done on the system is $-mRT$.

II. Remove reversibly through the wall permeable to B, n mols of B at the pressure Pb; work done being nRT.

IIa. Change the pressure from Pb to $P'b$ isothermally and reversibly. W_2, the work done is $nRT \log \frac{Pb}{P'b}$.

IIb. Introduce n mols of B at the pressure $P'b$ into II reversibly; work done on the system is $-nRT$.

III. In II, m mols of A and n mols of B at the pressures $P'a$ and $P'b$ respectively are allowed to combine to form p mols of C and q mols of D. No work is done in the conversion.

IV. p mols of C are withdrawn from II at the pressure $P'c$; work done being pRT.

IVa. The pressure is then changed isothermally and reversibly from $P'c$ to Pc. W_3, the work done is $pRT \log \frac{P'c}{Pc}$

IVb. p mols of C at the pressure Pc are then introduced into I; work done being $-pRT$.

---

* The boxes contain A, B, C and D in such large amounts that removal or addition of m, n, p and q mols of A, B, C and D respectively does not appreciably alter the partial pressures in the two boxes.

V. Similarly q mols of D are withdrawn from II at the pressure $P'd$; work done is qRT.

Va. The pressure is then changed from $P'd$ to Pd. W_4, the work done is $qRT \log \frac{P'd}{Pd}$.

Vb. q mols of D at the pressure Pd are introduced into I; work done being $- q$RT.

VI. In I, p mols of C and q mols of D are converted at the respective pressures Pc and Pd reversibly into m mols of A and n mols of B, to restore the original condition; no work is done in the conversion.

The work done in withdrawing A and B from I and introducing them into II, and the work done in withdrawing C and D from II and introducing them into I ($+ mRT - mRT$, $+ nRT - nRT$, $+ pRT$, $- pRT$, $+ qRT$ and $- qRT$) cancel each other. Since the original conditions are restored, the net work in the changes in pressures should be zero :

$$W_1 + W_2 + W_3 + W_4 = 0$$

$$\therefore \quad mRT \log \frac{Pa}{P'a} + nRT \log \frac{Pb}{P'b} + pRT \log \frac{P'c}{Pc} + qRT \log \frac{P'd}{Pd} = 0.$$

Collecting terms containing Pa, Pb, Pc and Pd, and $P'a$, $P'b$, $P'c$ and $P'd$ together, one gets,

$$RT \log Pa^m + RT \log Pb^n - RT \log Pc^p - RT \log Pd^q$$
$$- RT \log P'a^m - RT \log P'b^n + RT \log P'c^p + RT \log P'd^q$$

$$= RT \left\{ \log \frac{P'c^p \times P'd^q}{P'a^m \times P'b^n} \right\} + RT \left\{ \log \frac{Pa^m \times Pb^n}{Pc^p \times Pd^q} \right\} = 0$$

$$\therefore \quad \log \frac{P'c^p \times P'd^q}{P'a^m \times P'b^n} = \log \frac{Pc^p \times Pd^q}{Pa^m \times Pb^n}$$

$$\therefore \quad \frac{P'c^p \times P'd^q}{P'a^m \times P'b^n} = \frac{Pc^p \times Pd^q}{Pa^m \times Pb^n}.$$

This relation is valid for all values of pressures, provided A, B, C and D are in equilibrium.

$$\therefore \quad \frac{Pc^p \times Pd^q}{Pa^m \times Pb^n} = K,$$ and if K is determined in terms of pressures of the reacting substances, it is called K_p. As concentrations are proportional to pressures, one gets,

$$\frac{Cc^p \times Cd^q}{Ca^m \times Cb^n} = K_c.$$

The relation between Kc and K_p can be found by the application of gas laws.

$$\text{Since } PV = RT, \quad P = \frac{RT}{V} = RT \times C$$

$$\therefore \quad \frac{(RTCc)^p \times (RTCd)^q}{(RTCa)^m \times (RTCb)^n} = K_p.$$

$$\text{But} \quad \frac{Cc^p \times Cd^q}{Ca^m \times Cb^n} = K_c.$$

$$\therefore \quad \frac{(RT)^p \times (RT)^q}{(RT)^m \times (RT)^n} \times K_c = K_p;$$

$$\text{or} \quad K_c \times \frac{(RT)^{p+q}}{(RT)^{m+n}} = K_p$$

$$\text{or} \quad K_c \times (RT)^{(p+q\cdots)-(m+n\cdots)} = K_p.$$

If in the reaction $mA + nB...... \rightleftharpoons pC + qD.........$ any of the substances are not gaseous or in the condition of a dilute solution, their vapour pressures being constant, they may be neglected, in determining K_c or K_p.

21. The Effect of Temperature and Pressure on Chemical Equilibrium :—

The principle of *Le Chatelier* : If any constraint is applied to a system in equilibrium, the equilibrium is shifted in such a way as to annul the constraint. As rise of temperature applies constraint in the form of heat to a system, it favours reactions in which heat is absorbed and *vice versa.* As pressure reduces

volume, increase of pressure favours reactions in which there is a decrease in volume and *vice versa.* *e.g.* SO_2 and O_2 combine with a rise of temperature, *i.e.*, with production of heat. Fall of temperature favours and rise of temperature retards the formation of SO_3. In the combination of N_2 and H_2 to form NH_3, there is a decrease in volume, while in the decomposition of O_3 into O_2 there is an increase in volume. Pressure favours the first reaction and retards the second.

These conclusions follow from the application of the Law of Mass Action, to such reactions. Dissociation of PCl_5 will serve as an illustration.

In the reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2,$$

if a = gram molecules of PCl_5 initially present,

V = Volume which is kept constant during decomposition.

x = gram molecules of Cl_2 and PCl_3 formed,

the respective concentrations at equilibrium will be,

$$[Cl_2] = \frac{x}{V};$$

$$[PCl_3] = \frac{x}{V};$$

$$[PCl_5] = \frac{a-x}{V}.$$

According to the Law of Mass Action,

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\left(\frac{x}{V}\right)^2}{\left(\frac{a-x}{V}\right)}$$

$$= \frac{x^2}{(a-x)V}.$$

It will be seen that if V is increased $\frac{x^2}{(a-x)}$ must be increased to keep the value of K constant. x, the amount of dissociation, must therefore be greater. Increase of volume or decrease of pressure produces increase in the dissociation and *vice versa.*

In gases, partial pressures of the reacting substances are often used to represent the concentrations. The equation will have then the following form :—

$$K_p = \frac{(P_2)^2}{(P_1)};$$

where, P_1 = partial pressure of PCl_5
P_2 = partial pressure of PCl_3 and Cl_2, and
K_p = equilibrium constant.

When concentrations are used in the above equation, the constant obtained is called K_c and the relation

$$K_p = K_c(RT)^{(p+q\cdots)-(m+n\cdots)}$$

has already been given.

22. **Van't Hoff's Isotherm.**—

It gives the maximum work which can be obtained in a homogeneous chemical reaction, (a reaction occurring in gaseous systems) at constant temperature and volume in terms of the equilibrium constant, and the concentrations of the reacting substances and the concentrations of the products formed. The maximum work is a measure of the affinity of the reaction. In deriving the relation, the device of the 'Equilibrium Box' is used as in deriving the Law of Mass Action. The reaction,

$$A + B = C + D$$

is made to occur in the Equilibrium Box The 'Box' is supposed to have one wall permeable to A, a second one to B, a third one to C, and a fourth one to D. The reactants (A and B) and the products (C and D) are assumed to be perfect gases.

Let pa and pb be the initial partial pressures of A and B, and pc and pd be the final partial pressures of the products formed, and let $p'a$, $p'b$, $p'c$, and $p'd$, be their pressures at equilibrium.

(1) The pressure of A is changed from pa to $p'a$; the work done is RT $\log_e \frac{pa}{p'a}$.

(2) Similarly, the pressure of B is changed from pb to $p'b$, the work done is RT $\log_e \frac{pb}{p'b}$.

(3) The gases are introduced into the 'Equilibrium Box' through the respective permeable walls. Work done by the gas in the process is RT per mol. A and B at equilibrium pressures then react to form C and D at equilibrium pressures in the 'Equilibrium Box' and no work is done during the conversion.

(4) C and D are then removed from the 'Equilibrium Box' through the walls respectively permeable to them. Work done on the gas is RT per mol.

(5) C and D are then brought to their final pressures, the work done in the case of C is RT $\log_e \frac{p'c}{pc}$ and that in the case of D is RT $\log_e \frac{p'd}{pd}$.

The total work :—

$$W = RT \log_e \frac{pa}{p'a} + RT \log_e \frac{pb}{p'b} + RT \log_e \frac{p'c}{pc} + RT \log_e \frac{p'd}{pd}$$

$$= RT \{ \log_e p'c + \log_e p'd - \log_e p'a - \log_e p'b + \log_e pa + \log_e pb - \log_e pc - \log_e pd \}$$

$$= RT \left\{ \log_e \frac{p'c \times p'd}{p'a \times p'b} + \log_e \frac{pa \times pb}{pc \times pd} \right\}$$

or, $$= RT \log_e \frac{p'c \times p'd}{p'a \times p'b} - RT \log_e \frac{pc \times pd}{pa \times pb}.$$

But, $$\frac{p'c \times p'd}{p'a \times p'b} = K$$

$$\therefore \quad W = 2{\cdot}303 \text{ RT} \log K - 2{\cdot}303 \log \frac{pc \times pd}{pa \times pb}.$$

In general, when n_1 mols of A_1, n_2 mols of A_2, ... react reversibly to form $n'_1A'_1 + n'_2A'_2 + \ldots\ldots\ldots$,

$$W = 2{\cdot}303 \text{ RT} \log K - 2{\cdot}303 \text{ RT} \log \frac{[A'_1]^{n'_1}}{[A_1]^{n_1}} \frac{[A'_2]^{n'_2} \ldots\ldots}{[A_2]^{n_2} \ldots\ldots}$$

or, $\quad W = 2{\cdot}303 \text{ RT} \log K - 2{\cdot}303 \text{ RT} \Sigma\, n \log C.$

W is the maximum work obtained in a homogeneous chemical reaction, and the above equation is known as **van't Hoff's Isotherm.**

If all the reactants are taken at unit concentration (or unit pressure) and all the resultants obtained are at unit concentration (or unit pressure) the second term disappears, and the isotherm becomes,

$$W = 2{\cdot}303 \text{ RT} \log K.$$

The equation assumes that in the reaction, the number of mols that react are equal to those that result, or that the reaction is carried out at constant volume. If however, that is not the case, and if

the resultant molecules $-$ the reactant molecules $= n$,

the work done in the change of volume must be taken into consideration, and the equation then becomes :

$$W = 2{\cdot}303 \text{ RT} \log K + n\text{RT}.$$

$$\therefore \quad W - n\text{RT} = 2{\cdot}303 \text{ RT} \log K.$$

If Δ is the change in the free energy, then,

$$\Delta F = W - n\text{RT} = 2{\cdot}303 \text{ RT} \log K.$$

23. Van't Hoff's Isochore.—

It summarises the influence of temperature on equilibrium constant, and can be derived from the Isotherm.

At constant volume, $W = \text{RT} \log_e K$, and taking $W = A$ (the change in the free energy)

$$A = RT \log_e K.$$

Differentiating with respect to T and K,

$$dA = R \log_e K \, dT + RT \, d \log_e K.$$

On multiplying by $\frac{T}{dT}$ one gets,

$$T \cdot \frac{dA}{dT} = RT \log_e K + RT^2 \frac{d \log_e K}{dT};$$

but $A - U = T \frac{dA}{dT}$ (Gibb's Helmholtz's Equation) and if Q, the heat evolved, represents U, the total diminution in the energy, $A - Q = T \cdot \frac{dA}{dT}$.

$$\therefore \quad A - Q = RT \log_e K + RT^2 \frac{d \log_e K}{dT}$$

but, $A = RT \log_e K$

$$\therefore \quad -Q = RT^2 \frac{d \log_e K}{dT},$$

or

$$\frac{d \log_e K}{dT} = -\frac{Q}{RT^2}.$$

Integrating between K_1, K_2 and T_1, T_2 one gets,

$$\log_e K_2 - \log_e K_1 = \frac{-Q}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right).$$

Changing logs to the base 10,

$$\log \frac{K_2}{K_1} = \frac{-Q}{2 \cdot 303 \, R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

This is van't Hoff's Isochore. In the above formula K_1 and K_2 are the equilibrium constants at T_1 and T_2, Q is the heat of the reaction at constant volume, and $R = 1 \cdot 985$ calories.

24. Unimolecular Reactions*.—

A unimolecular reaction can be represented as,

$$A \longrightarrow B + C + \ldots\ldots$$

---

* It is assumed that products formed react to a very small extent and the reactions therefore may be supposed to run only in one direction.

If a is the initial concentration of A and x the amount transformed after a time t, then by the law of mass action,

$$\frac{dx}{dt} = K(a - x)$$

$$\text{or} \quad \frac{dx}{a - x} = Kdt.$$

On integration,

$$-\log_e(a - x) = Kt + C. \quad \text{Where C is a constant.}$$

The value of C can be determined by making $t = 0$, when $x = 0$.

$$C = -\log_e a$$

Putting this value in the above equation, one gets

$$-\log_e(a - x) = Kt - \log_e a$$

$$\log_e a - \log_e(a - x) = Kt$$

$$\frac{1}{t}\log_e \frac{a}{(a - x)} = K$$

$$\text{or,} \quad K = \frac{2{\cdot}303}{t}\log\frac{a}{a - x}$$

If x_1 and x_2 are the amounts transformed after time intervals t_1 and t_2 respectively, then,

$$2{\cdot}303 \log\frac{a}{a - x_1} = Kt_1$$

$$\text{and} \quad 2{\cdot}303 \log\frac{a}{a - x_2} = Kt_2.$$

Subtracting the former from the latter,

$$2{\cdot}303 \log\frac{a - x_1}{a - x_2} = K(t_2 - t_1)$$

$$\text{or,} \quad \frac{2{\cdot}303}{t_2 - t_1}\log\frac{a - x_1}{a - x_2} = K.$$

In unimolecular reactions, the value of K (velocity constant) is independent of the unit chosen for concentration.

25. Bimolecular Reactions*.—

The reaction may be written as,

$$A + B \longrightarrow C + D + E + \ldots\ldots$$

(i) The initial concentrations of both A and B are equal. Let the initial concentrations be a and let x be the amount of both A and B transformed in time t, then

$$\frac{dx}{dt} = K(a - x)^2$$

Integrating one gets,

$$K = \frac{1}{at} \cdot \frac{x}{a - x}.$$

(ii) The initial concentrations of A and B are different, that of A being 'a' and that of B being 'b'.

Then, $$\frac{dx}{dt} = K(a - x)(b - x).$$

To facilitate integration, the equation may be written as follows :—

$$\frac{dt}{dx} = \frac{1}{K(a - x)(b - x)}$$

$$\frac{dt}{dx} = \frac{1}{K(a - b)} \cdot \left(\frac{1}{b - x} - \frac{1}{a - x}\right)$$

$$dt \cdot K(a - b) = dx\left(\frac{1}{b - x} - \frac{1}{a - x}\right)$$

$$= dx\left[(b - x)^{-1} - (a - x)^{-1}\right]$$

$$\int dt \cdot K(a - b) = \int dx\left[(b - x)^{-1} - (a - x)^{-1}\right]$$

$$= \int dx(b - x)^{-1} - \int dx(a - x)^{-1}$$

$$t \cdot K(a - b) = -\log_e(b - x) + \log_e(a - x) + C$$

$$= \log_e \frac{a - x}{b - x} + C.$$

* It is assumed that products formed react to a very small extent and the reactions therefore may be supposed to run only in one direction.

The value of C can be found by putting $x = 0$, when, $t \cdot K(a - b)$ will also be equal to zero.

$$0 = \log_e \frac{a}{b} + C$$

or,
$$C = -\log_e \frac{a}{b}.$$

Putting this value in the above equation,

$$t \cdot K(a - b) = \log_e \frac{a - x}{b - x} - \log_e \frac{a}{b}$$

$$= \log_e \frac{b(a - x)}{a(b - x)}.$$

Therefore,
$$K = \frac{1}{t(a - b)} \log_e \frac{b(a - x)}{a(b - x)}$$

$$= \frac{2 \cdot 303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}.$$

For a bimolecular reaction, the value of K depends on the unit of concentration chosen. If a unit is $\frac{1}{n}$th of the unit used, the equation becomes :—

$$K' = \frac{2 \cdot 303}{tn(a - b)} \log \frac{nb \cdot n(a - x)}{na \cdot n(b - x)}$$

$$nK' = \frac{2 \cdot 303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

or, $K = nK'$.

26. **The Order of a Reaction.**—

(1) *Direct method* :—Determine the changes in the concentration of the substances taking part in the reaction with time and substitute the values of the concentration and those of the corresponding time in the different equations, on the assumption that it is unimolecular, bimolecular or of a higher order and determine the constants. The order of the reaction is shown by the equation which gives the best constant.

(2) Calculate the time taken to alter the original concentrations of the reacting substances to one half of their value.

(i) In a unimolecular reaction when $x = \frac{a}{2}$

$$K = \frac{1}{t}\log\frac{a}{a-x}$$

$$= \frac{1}{t}\log\frac{a}{a-\frac{a}{2}}$$

$$= \frac{1}{t}\log 2$$

or, $$t = \frac{1}{K}\log 2$$

The time required is independent of the original concentration.

(ii) In a bimolecular reaction when $x = \frac{a}{2}$

$$K = \frac{1}{t}\cdot\frac{x}{a(a-x)}$$

$$= \frac{1}{t}\cdot\frac{\frac{a}{2}}{a\left(a-\frac{a}{2}\right)}$$

$$= \frac{1}{t}\cdot\frac{1}{a}$$

or, $$t = \frac{1}{K}\cdot\frac{1}{a}.$$

The time required is inversely proportional to the initial concentrations.

In general, for a reaction of the nth order, the time ($t_{\frac{1}{2}}$) required for half decomposition is inversely proportional to the ($n-1$)th power of the initial concentration,

or, $$t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}.$$

Carry out the reaction with two different initial concentrations a_1 and a_2. If t_1 and t_2 are the times required for half decomposition,

$$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}}$$

$$\log \frac{t_1}{t_2} = (n - 1) \log \frac{a_2}{a_1}$$

$$\frac{\log \frac{t_1}{t_2}}{\log \frac{a_2}{a_1}} + 1 = n.$$

(3) Graphical Method :

(i) The equation for unimolecular reaction is,

$$K = \frac{1}{t} \log \frac{a}{a - x}$$

$$Kt = \log a - \log (a - x).$$

This is of the form $y = C - mx$ which is the equation for a straight line.

∴ for a unimolecular reaction when t is plotted against $\log (a - x)$, the graph should be a straight line.

(ii) The equation for a bimolecular reaction is,

$$K = \frac{1}{t} \cdot \frac{x}{a(a - x)}$$

$$aKt = \frac{x}{a - x}$$

$$K't = \frac{x}{a - x}$$

$$\frac{1}{tK'} = \frac{a}{x} - 1.$$

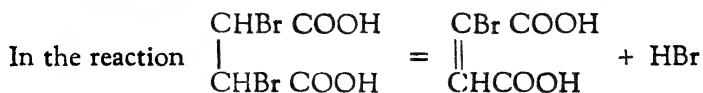
If a straight line is obtained, when t is plotted against $\frac{x}{a - x}$ or when $\frac{1}{t}$ is plotted againtst $\frac{a}{x}$, then the reaction is bimolecular.

(4) If two or more substances take part in a reaction, the order with respect to each substance can be determined by any of

the above methods, provided all the other substances are taken in sufficiently large amounts so that their concentrations do not appreciably change during the course of the reaction.

27. **Relation between Temperature and Velocity of a Reaction.**—(i) Arrhenius suggested an empirical formula to represent this relation. It is found that for an increase of 10° in temperature, velocity increases two to three times.

In the reaction

$$\begin{matrix} CHBr\,COOH \\ | \\ CHBr\,COOH \end{matrix} = \begin{matrix} CBr\,COOH \\ \| \\ CHCOOH \end{matrix} + HBr$$

the velocity constants at 40°, 50°, 70° and 80°C are 0·0000863, 0·000249, 0·00169, and 0·0046 respectively.

$$\frac{K50^\circ}{K40^\circ} = \frac{0{\cdot}000249}{0{\cdot}0000863}$$

$$= 2{\cdot}88$$

and

$$\frac{K80^\circ}{K70^\circ} = \frac{0{\cdot}0046}{0{\cdot}00169}$$

$$= 2{\cdot}72.$$

The increase in the kinetic energy for 10°C. rise $\approx 3\%$ and cannot explain the great rise in the velocity. The temperature increases in arithmetical progression, while velocity of the reaction increases approximately in geometrical progression, (the increase between 40°C. and 50°C. is 2·88 and that between 70°C. and 80°C. is 2·72). Arrhenius therefore suggested,

$$\log K = -\frac{A}{T} + B,$$

where K = velocity constant;
T = Temperature;
A and B are constants.

On differentiation, the expression assumes the following form :—

$$\frac{d \log K}{dt} = \frac{-E}{R} \cdot \frac{1}{T^2}$$

where A is taken to be $= \frac{E}{R}$.

On integration between the limits K_1 and K_2, and T_1 and T_2, it gives

$$\log K_1 - \log K_2 = \frac{-E}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right).$$

Arrhenius considered E as the *activation energy* which the reacting molecules must possess before they react. A certain fraction of the molecules favourably situated gets this energy from the rise in temperature.

(ii) The relation can be derived from the kinetic energy of the molecules and Maxwell's law of the distribution of velocities. (It is assumed that collisions between molecules is necessary for reaction.)

Z, the number of collisions between molecules in one c. c. in one second $= \sqrt{2}\ \pi \sigma^2 u n^2$

where σ = the effective diameter of the molecules,
u = the mean square root velocity,
n = the number of molecules in one c. c.

According to Maxwell's law of the distribution of velocities, the fraction of molecules at T, which possess the activation energy E, is $e\left(\frac{-E}{RT}\right)$ (e is the base of natural log) and as only this fraction reacts on collision,

$$\text{the velocity } \frac{dx}{dt} = Z \times e\left(\frac{-E}{RT}\right).$$

But $\frac{dx}{dt} = Kn^2$ $\quad \therefore\ Kn^2 = Z \times e\left(\frac{-E}{RT}\right);$

$$= (\sqrt{2}\ \pi \sigma^2 u)\, n^2 \times e\left(\frac{-E}{RT}\right)$$

$$\therefore\ K = (\sqrt{2}\ \pi \sigma^2 u) \times e\left(\frac{-E}{RT}\right).$$

But for a small change in temperature, u does not appreciably alter and $\sqrt{2}\ \pi\Omega^2 u$ is approximately constant.

$$\therefore \quad K \propto e^{\frac{-E}{RT}}$$

$$\therefore \quad \frac{d \log_e K}{dt} = \frac{-E}{RT^2}$$

which gives on integration, $\log K_1 - \log K_2 = \frac{-E}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$

(iii) The relation can be derived from van't Hoff's Isochore.

$$\frac{d \log_e K}{dt} = \frac{-Q}{RT^2}$$

Q, the heat of the reaction may be taken as the difference $q - q'$, q being the heat of the forward reaction and q', the heat of the backward reaction. The equilibrium constant K is the ratio of the velocity constants, k, of the forward reaction and k_1, of the backward reaction.

$$\therefore \quad \frac{d \log \frac{k}{k_1}}{dt} = \frac{-(q - q')}{RT^2}$$

$$\therefore \quad \frac{d \log k}{dt} = \frac{-q}{RT^2}$$

$$\text{and} \quad \frac{d \log k_1}{dt} = \frac{q'}{RT^2} .$$

Considering only the forward reaction, q becomes the activation energy of the reacting molecules and one gets :—

$$\frac{d \log k}{dt} = \frac{-q}{RT^2} = \frac{-E}{RT^2}$$

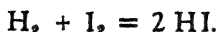
which on integration gives,

$$\log k_1 - k_2 = \frac{-E}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

Problems with solutions

Problem 137. When 5·71 mols of iodine and 6·22 mols of hydrogen are heated to 357°C. till the equilibrium is established, 9·55 mols of hydriodic acid are formed. Calculate the equilibrium constant.

Solution : The reaction takes place according to the equation,

$$H_2 + I_2 = 2\,HI.$$

$\therefore$ to form 9·55 mols of HI, 4·775 mols of H_2 and 4·775 mols of I_2 are used up. At equilibrium the respective concentrations will be,

$$H_2,\ (6{\cdot}22 - 4{\cdot}775) = 1{\cdot}445 \text{ mols.}$$

$$I_2,\ (5{\cdot}710 - 4{\cdot}775) = 0{\cdot}935 \text{ mols.}$$

$$2\,HI = 9{\cdot}55 \text{ mols.}$$

$$\text{The equilibrium constant } K = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$= \frac{(4{\cdot}775)^2}{(1{\cdot}445)\,(0{\cdot}935)}.$$

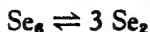
$$\therefore\quad K = 16{\cdot}880.$$

As there is no change in the number of molecules, the volume does not come into consideration.

Ans. The equilibrium constant is 16·880.

Problem 138. Selenium (Se) dissociates according to the equation $Se_6 \rightleftharpoons 3\,Se_2$; 0·0755 g of Se at 700°C. and 185 mm. pressure was found to occupy a volume of 114·2 c. c. Calculate the degree of dissociation and the equilibrium constant K_p.

Solution : (1) From the equation

$$Se_6 \rightleftharpoons 3\,Se_2$$

if x be the degree of dissociation, the total number of mols at the equilibrium will be $1 + 2x$. The apparent molecular weight M') of Se will be found by the equation

$$PV = nRT.$$

Expressing P and V in atmospheres and litres respectively, one gets

$$\frac{185}{760} \times 0{\cdot}1142 = \frac{0{\cdot}0755 \times 0{\cdot}08204 \times 973}{M^1}.$$

$$\therefore \quad M^1 = \frac{0{\cdot}0755 \times 0{\cdot}08204 \times 973 \times 760}{185 \times 0{\cdot}1142}$$

$$= 216{\cdot}9.$$

Then, $216{\cdot}9\,(1 + 2x) = 473{\cdot}76$ (Mol. wt. of $Se_6 = 473{\cdot}76$)

$$\therefore \quad 1 + 2x = \frac{473{\cdot}76}{216{\cdot}9}$$

$$= 2{\cdot}186.$$

$$\therefore \quad x = \frac{2{\cdot}186 - 1}{2} = \frac{1{\cdot}186}{2}$$

$$= 0{\cdot}593.$$

The degree of dissociation is, therefore, 0·593.

(2) To find the equilibrium constant K_p, first calculate the pressure of Se_2 and Se_6.

$$\text{The pressure (of } x \text{ mol) of } Se_2 = \frac{0{\cdot}593 \times 185}{2{\cdot}186}$$

$$= 50{\cdot}20 \text{ mm.}$$

$$\text{The pressure (of } 1 - x \text{ mol) of } Se_6 = \frac{0{\cdot}407 \times 185}{2{\cdot}186}$$

$$= 34{\cdot}45 \text{ mm.}$$

$$\therefore \quad K_p = \frac{\left(\dfrac{50{\cdot}20}{760}\right)^3}{\left(\dfrac{34{\cdot}45}{760}\right)}$$

$$= \frac{(50{\cdot}20)^3}{(760)^2 \times 34{\cdot}45}$$

$$= 0{\cdot}006357.$$

Ans. (1) Degree of dissociation = 0·593.
(2) Equilibrium constant = 0·006357.

Problem 139. The dissociation pressure of NH_4I at 440°C. is 1870 mm., the vapour consisting entirely of NH_3 and HI. If the vapour is kept at this temperature, the pressure rises to p, owing to the reaction, $2HI = H_2 + I_2$. If $K = \frac{pH_2 \, pI_2}{p^2HI} = 0{\cdot}0198$, calculate p.

Solution : The pressure of 1870 mm. (say P) is equally divided between NH_3 and HI.

$$\therefore \quad pNH_3 \cdot pHI = \frac{P^2}{4}.$$

If x be the increase in pressure, the new pressure of NH_3 will be $\frac{P + x}{2}$ and that of undissociated HI will be

$$\frac{P^2}{4} \times \frac{2}{P + x} \text{ or } \frac{P^2}{2(P + x)}.$$

$\frac{P + x}{2} - \frac{P^2}{2(P + x)}$ *i. e.*, the difference of the pressure of total HI formed by the dissociation of NH_4I and that of undissociated HI, is again shared equally by H_2 and I_2. Therefore, their individual pressures will be

$$\frac{1}{4}\left[\frac{(P + x)^2 - P^2}{(P + x)}\right].$$

$$\text{Then,} \qquad \frac{pH_2 \, pI_2}{p^2 \, HI} = \frac{\left\{\frac{1}{4}\left[\frac{(P + x)^2 - P^2}{(P + x)}\right]\right\}^2}{\left\{\frac{P^2}{2(P + x)}\right\}^2}$$

$$= \frac{\frac{1}{4}\left[(P + x)^2 - P^2\right]^2}{P^4} = K.$$

$$\therefore \quad \frac{\left[(P + x)^2 - P^2\right]^2}{P^4} = 4K.$$

$$\therefore \quad \frac{(P + x)^2 - P^2}{P^2} = 2\sqrt{K}$$

$$\frac{(P + x)^2}{P^2} = 2\sqrt{K} + 1$$

$$(P + x)^2 = (2\sqrt{K} + 1) P^2$$

$$P + x = (2\sqrt{K} + 1)^{\frac{1}{2}} P.$$

$(P + x)$ is the final pressure, which can be calculated (without finding the value of x) by substituting the values of K and P in the right hand side of the above equation :

$$P + x = [2(0{\cdot}0198)^{\frac{1}{2}} + 1]^{\frac{1}{2}} \times 1870$$

$$= 1{\cdot}132 \times 1870$$

$$= 2117 \text{ mm.}$$

Ans. The final pressure is 2117 mm.

Problem 140. The vapour pressure of solid NH_4CN at 11°C. is 22·7 cms. Assuming that the vapour is practically completely dissociated into NH_3 and HCN (i) what will the partial pressure of HCN if solid NH_4CN is sublimed at 11°C. in a closed vessel, filled with NH_3 at a pressure of 32·28 cms. and (ii) what will be the total final pressure ?

Solution : According to the law of mass action,

$$\frac{pNH_3 \; pHCN}{pNH_4CN} = K.$$

But so long as solid NH_4CN is present, pNH_4CN remains constant, and then the above equation becomes,

$$pNH_3 \; pHCN = K'.$$

$$pNH_3 \; pHCN = (11{\cdot}35)^2,$$

$\because \quad pNH_3 = 11{\cdot}35$ and $pHCN = 11{\cdot}35$.

Let x be the partial pressure of HCN when NH_3 is present at 32·28 cms. Then the total pressure of NH_3 in the vessel will be, $32{\cdot}28 + x$; and

$$(32{\cdot}28 + x)(x) = (11{\cdot}35)^2$$
$$x^2 + 32{\cdot}28x = (11{\cdot}35)^2$$
$$x^2 + 32{\cdot}28x + (16{\cdot}14)^2 = (11{\cdot}35)^2 + (16{\cdot}14)^2$$
$$(x + 16{\cdot}14)^2 = (19{\cdot}73)^2$$
$$\therefore \quad x + 16{\cdot}14 = 19{\cdot}73$$
$$x = 19{\cdot}73 - 16{\cdot}14$$
$$= 3{\cdot}59$$

Ans. (i) The partial pressure of HCN in the presence of NH_3 at 32·28 cms. will be 3·59 cms.

(ii) The final pressure will be
(32·28 + 3·59 + 3·59 =) 39·46 cms.

Problem 141. A mixture containing initially 49 % HCl and 51 % O_2 was caused to react under the influence of a catalyst at a pressure of 723 mm. and at 480°C. The fraction of HCl transformed was 0·76. Calculate the equilibrium constant K_p (P in atmospheres).

Solution : Find the initial concentration in mols / *l* by using the general gas formula PV = *n*RT

$$\text{or} \quad \frac{n}{V} = \frac{P}{RT}$$

$$= \frac{723}{760 \times 0{\cdot}08204 \times 753}$$

$$= 0{\cdot}0154 \text{ mols} / l.$$

mol of HCl = 0·0154 × 0·49 = 0·007546.

mol of O_2 = 0·0154 × 0·51 = 0·007854.

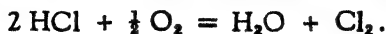
mol of HCl transformed = 0·007546 × 0·76

= 0·005735.

mol of O_2 required for this transformation,

= 0·001434

i. e., one fourth of HCl mols, as per equation :

$$2\,HCl + \tfrac{1}{2}\,O_2 = H_2O + Cl_2.$$

At the equilibrium, the mols present are :

$$HCl,\ 0{\cdot}007546 - 0{\cdot}005735 = 0{\cdot}001811$$

$$O_2,\ 0{\cdot}007854 - 0{\cdot}001434 = 0{\cdot}006420$$

$$H_2O,\ (2 \times \text{mols of } O_2 \text{ used}) = 0{\cdot}002867$$

$$Cl_2,\ (\quad ,, \quad) = 0{\cdot}002867$$

total number of molecules = 0·013965.

The pressure in atmospheres per mol,

$$= \frac{723}{763 \times 0{\cdot}013965} = 68{\cdot}19 \text{ atmospheres.}$$

The individual pressures will be,

$$HCl = 0{\cdot}001811 \times 68{\cdot}19$$

$$O_2 = 0{\cdot}006420 \times 68{\cdot}19$$

$$H_2O = 0{\cdot}002867 \times 68{\cdot}19$$

$$Cl_2 = 0{\cdot}002867 \times 68{\cdot}19.$$

The equilibrium constant will be,

$$K_p = \frac{pH_2O\ pCl_2}{p^2HCl\ p^{\frac{1}{2}}O_2}$$

$$= \frac{(0{\cdot}002867 \times 68{\cdot}19)(0{\cdot}002867 \times 68{\cdot}19)}{(0{\cdot}001811 \times 68{\cdot}19)^2(0{\cdot}006420 \times 68{\cdot}19)^{\frac{1}{2}}}$$

$$= 3{\cdot}789.$$

Ans. The equilibrium constant K_p is 3·789.

Problem 142. The value of the equilibrium constant $K_c = \frac{[HCl]^2}{[H_2][Cl_2]}$ at 900°T is $10^{11{\cdot}4^\circ}$, and the fractional dissociation of water vapour at the same temperature and at 1 atmosphere pressure is $10^{-7{\cdot}49}$. Calculate for this temperature

the Deacon reaction constant $K_p = \dfrac{p^2H_2O\ p^2Cl_2}{pO_2\ p^4HCl}$, pressure being expressed in atmospheres.

Solution: Find the equilibrium constant K_{c_1} for water vapour by the formula $PV = nRT$.

If P is 1 atmosphere, and V in litres,

$$\text{then} \quad n = \frac{1}{RT} = \frac{1}{0{\cdot}08204 \times 900}$$

$$= 0{\cdot}01355 \text{ mols per litre.}$$

As the fractional dissociation is $10^{-7\cdot49}$ at the equilibrium of the dissociation, $2H_2O \rightleftharpoons 2H_2 + O_2$.

$$H_2 \text{ mol} = 1{\cdot}355 \times 10^{-2} \times 10^{-7\cdot49}$$

$$O_2 \text{ mol} = 0{\cdot}678 \times 10^{-2} \times 10^{-7\cdot49}$$

$$H_2O \text{ mol} = 1{\cdot}355 \times 10^{-2} - 1{\cdot}355 \times 10^{-2} \times 10^{-7\cdot49}$$

$= 1{\cdot}355 \times 10^{-2}(1 - 10^{-7\cdot49})$, but for calculations, $1{\cdot}355 \times 10^{-2}$ may be taken.

The equilibrium constant for water

$$K_{c_1} = \frac{[H_2]^2\,[O_2]}{[H_2O]^2}.$$

$$= \frac{(1{\cdot}355 \times 10^{-9\cdot49})^2\,(6{\cdot}78 \times 10^{-10\cdot49})}{(1{\cdot}355 \times 10^{-2})^2}$$

$$= 6{\cdot}78 \times 10^{-14\cdot98} \times 10^{-10\cdot49}$$

$$= 6{\cdot}78 \times 10^{-25\cdot47}.$$

$$K_c = \frac{[HCl]^2}{[H_2]\,[Cl_2]} = 10^{11\cdot40} \quad \dots \quad \dots \quad (A).$$

$$K_{c_1} = \frac{[H_2]^2\,[O_2]}{[H_2O]^2} = 6{\cdot}78 \times 10^{-25\cdot47} \quad \dots \quad (B).$$

Multiplying B by A^2,

$$K_{c_2} = \frac{[HCl]^4\,[O_2]}{[H_2O]^2\,[Cl_2]^2} = 6{\cdot}78 \times 10^{-25\cdot47} \times 10^{22\cdot80}.$$

To convert gm mols / l into pressure, multiply each term of the above equation by RT or $0{\cdot}08204 \times 900$. Then

$$K_{p1} = \frac{p^4HCl\ pO_2}{p^2H_2O\ p^2Cl_2} = 6{\cdot}78 \times 10^{-2.67} \times 0{\cdot}08204 \times 900$$

$$= 500{\cdot}5 \times 10^{-2.67}$$

or $$= 0{\cdot}5005 \times 10^{0.33}.$$

But $$K_{p1} = \frac{1}{K_p},$$

$$\therefore \quad K_p = \frac{1}{K_{p1}}.$$

$$\therefore \quad K_p = \frac{p^2H_2O\ p^2Cl_2}{p^4HCl\ pO_2} = \frac{1}{0{\cdot}5005 \times 10^{0.33}}$$

$$= 1{\cdot}998 \times 10^{-0.33}.$$

Ans. The reaction constant $K_p = 1{\cdot}998 \times 10^{-0.33}$.

Problem 143. At 2000°C. the equilibrium constant for pressures in atmospheres for the reaction $CO + \frac{1}{2}O = CO_2$ is $1{\cdot}07 \times 10^2$. What is the maximum work obtainable by the formation at 2000° of one gram molecule of CO_2 at atmospheric pressure from one gram molecule of CO and ½ gram molecule of O_2, both at atmospheric pressure ?

Solution : The maximum work can be obtained by the use of van't Hoff's Isotherm which is expressed by the equation,

$$A = RT \log_e K - RT \log_e \frac{pd\ pc}{pa\ pb}$$

for a reaction $A + B \rightleftharpoons C + D$, where K is the equilibrium constant and pd, pc, pa and pb are pressures of the reacting substances (gases). Since there is no change in pressure as a result of the reaction, the second term of the Isotherm disappears.

$$\therefore \quad A = RT \log_e K.$$

$$= 2{\cdot}302\ RT \log K$$

Substituting the values, we get,

$$A = 2{\cdot}302 \times 1{\cdot}985 \times 2273 \log 1{\cdot}07 \times 10^2$$

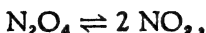
$$= 2{\cdot}302 \times 1{\cdot}985 \times 2273 \times 2{\cdot}0294$$

$$= 21078 \text{ cals.}$$

Ans. The maximum work = 21078 cals.

Problem 144. The vapour density of nitrogen peroxide at 27°C. is 38·33 (H = 1) and at 111°C. it is 23·83. Calculate its (i) degree of dissociation and (ii) the equilibrium constants at these temperatures, and (iii) the heat of dissociation at the mean temperature of 69°.

Solution : Nitrogen peroxides dissociates according to the equation,

$$N_2O_4 \rightleftharpoons 2\,NO_2,$$

The apparent molecular weight from the density will be

$$38{\cdot}33 \times 2 = 76{\cdot}66.$$

If a be the degree of dissociation, then

$$76{\cdot}66\,(1 + a) = 92.$$

$$\therefore \quad a = \frac{92}{76{\cdot}66} - 1$$

$$= 1{\cdot}2 - 1$$

$$= 0{\cdot}2.$$

To find the equilibrium constant, first calculate the volume (in litres) of 1·2 mols at 27°C.,

$$v = \frac{300 \times 22{\cdot}4 \times 1{\cdot}2}{273}$$

$$= 29{\cdot}54.$$

The equilibrium constant $K = \dfrac{[NO_2]\,[NO_2]}{[N_2O_4]}$

$$= \frac{\dfrac{a}{v} \times \dfrac{a}{v}}{\dfrac{(1 - a)}{v}}$$

$$= \frac{a^2}{v\,(1 - a)}$$

where, a = degree of dissociation ; v = volume in litres. Substituting the values of a and v in the above, one gets

$$K = \frac{(0 \cdot 2)^2}{29 \cdot 54 \times 0 \cdot 8}$$

$$= 0 \cdot 0016927$$

$$\text{or} \quad = 0 \cdot 0017.$$

(i) The degree of dissociation at 27°C. is 0·2 and

(ii) The equilibrium constant at this temperature is 0·0017 (K_1).

Similarly by using the same equations for 111°C.,

(i) The degree of dissociation = 0·9304 and

(ii) The equilibrium constant = 0·2034. (K_2)

(iii) The heat of dissociation at the mean temperature 69°C. is calculated by using van't Hoff's Isochore

$$Q = \frac{2 \cdot 302 \times R \times T_1 T_2}{T_2 - T_1} \log \frac{K_1}{K_2}$$

$$= \frac{2 \cdot 302 \times 1 \cdot 985 \times 384 \times 300}{(384 - 300)} \log \frac{0 \cdot 0017}{0 \cdot 2034}$$

$$= - \frac{2 \cdot 302 \times 1 \cdot 985 \times 384 \times 300 \times 2 \cdot 0779}{84}$$

$$= - 13050.$$

Ans. (i) The degree of dissociation at 27°C. 0·20

„ „ „ at 111°C. 0·9304

(ii) The equilibrium constant K_1 at 27°C. 0·0017

„ „ „ K_2 at 111°C. 0·2034

(iii) The heat of dissociation at the mean temperature (69°C.), – 13050 cals.

Problem 145. Potassium persulphate and potassium iodide interact with liberation of iodine. 25 c. c. of a solution which was $\frac{N}{30}$ with respect to both persulphate and iodide, were titrated from time to time with $\frac{N}{100}$ $Na_2S_2O_3$. From; the following

results show that the reaction is bimolecular. t is time in minutes and x the number of c. c.s of thiosulphate required.

t	9	16	32	50
x	4·52	7·80	14·19	20·05

Solution : The initial concentration or, final titration $= \frac{100 \times 25}{30}$

$= 83{\cdot}33$ c. c.s.

The velocity constant formula for the bimolecular reaction is,

$$K = \frac{1}{t} \cdot \frac{x}{a(a-x)}.$$

Substituting the respective values of a, x and t, the values of the constant K are calculated, which should nearly be the same.

$$K = \frac{1}{9} \cdot \frac{4{\cdot}52}{83{\cdot}33\,(83{\cdot}33 - 4{\cdot}52)} = 7{\cdot}647 \times 10^{-5}.$$

$$K = \frac{1}{16} \cdot \frac{7{\cdot}8}{83{\cdot}33\,(83{\cdot}33 - 7{\cdot}80)} = 7{\cdot}7455 \times 10^{-5}.$$

$$K = \frac{1}{32} \cdot \frac{14{\cdot}19}{83{\cdot}33\,(83{\cdot}33 - 14{\cdot}19)} = 7{\cdot}696 \times 10^{-5}.$$

$$K = \frac{1}{50} \cdot \frac{20{\cdot}05}{83{\cdot}33\,(83{\cdot}33 - 20{\cdot}05)} = 7{\cdot}605 \times 10^{-5}.$$

Ans. The values for constant K are nearly the same. The reaction is, therefore, a bimolecular one.

Problems for Solution

Problem 146. What is the theoretical amount of acetic ester formed from (a) one gram molecule of ethyl alcohol, and (b) from eight gram molecules of ethyl alcohol (K = 4).

Ans. (a) 66·6 per cent. (b) 96·6 per cent.

Problem 147. The value of the constant for the saponification of ethyl acetate is 6·94 at 25°C., concentrations being expressed in gram molecules per litre and times in minutes. In what time will $\frac{1}{3}$ of the ester be saponified if equal volumes of $\frac{N}{20}$ ethyl acetate and $\frac{N}{20}$ caustic soda are mixed at 25°C.

Ans. 1·441 minutes.

Problem 148. A bottle contains 500 c. c. of 50% alcohol. If 5 grams of ethyl acetate are added, how many grams of acetic acid must also be added to preserve the equilibrium. (The equilibrium constant of ethyl acetate is 4).

Ans. 2·178 grams.

Problem 149. The molecular weight of PCl_5 is 208. It dissociates into PCl_3 and Cl_2.. At 182°C. its density is 73·5 and at 220°C., it is 62. Find the degree of dissociation at the respective temperatures.

Ans. Temperature	Dissociation
182°C.	41·6 per cent.
220°C.	67·8 per cent.

Problem 150. The degree of dissociation of 1 original molecule of hydrogen iodide at 450°C. and one atmospheric pressure is 0·2198. Calculate the dissociation constants K_p and K_c. Also, show that the degree of dissociation is unaffected by the change of volume, and find the partial pressure of I_2 when the volume of the equilibrium mixture is doubled.

Ans. (i) $K_p = K_c = 0{\cdot}01988$. (ii) $P = 0{\cdot}05495$.

Problem 151. In four experiments in which one gram molecule of acetic acid was allowed to react with the following different quantities (*x* gram molecules) of ethyl alcohol while equilibrium was established. It was found that the following amounts of ethly acetate (*y* gram molecules) were produced.

	I	II	III	IV
x	0·5	1·0	2·0	12·0
y	0 42	0·66	0·83	0·98

Show that these results are in accord with the law of mass action.

Ans.

$$K = \frac{C_{\text{ester}} \cdot C_{\text{water}}}{C_{\text{acid}} \cdot C_{\text{alcohol}}}.$$

I K = 3·800. III K = 3·464
II K = 3·946. IV K = 4·337

Problem 152. Natausan obtained the following numbers for the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ at 21°. Calculate for each pressure (i) the percentage dissociation of N_2O_4 (ii) the partial pressures of N_2O_4 and NO_2 respectively, (iii) the equilibrium constant.

Pressure in mm.	43·58	101·64	230·6	492·1	617·6
Density (Air = 1)	2·049	2·283	2·501	2·684	2·722

The vapour density of NO_2 = 1·589 (Air = 1).

Ans. (i) The percentage dissociation :

55·09 39·20 27·07 18·40 16·75.

(ii) Partial pressures

N_2O_4	12·62	44·39	132·4	339·1	440·4,
NO_2	30·96	57 25	98·2	153·0	177·2.

(iii) The equilibrium constant

$$K = \frac{[NO_2]^2}{[N_2O_4]},$$

75·9 73·8 72·9 69·0 71·3.

Problem 153. If nitrogen peroxide is half dissociated under certain conditions, what proportion will remain undissociated when the volume is increased to ten times the original value, while the temperature remains the same.

Ans. 14·6 per cent.

Problem 154. Bodenstein found that at 443° the dissociation of hydrogen iodide according to the equation,

$$2\,HI \rightleftharpoons H_2 + I_2,$$

was 21·98 per cent. For experiments at the same temperature starting with varying amounts of hydrogen and iodine, the amount of hydrogen iodide present when equilibrium was attained is given by the following numbers :—

Iodine (c. c. vapour) initial	2·94	5·30	9·27	14·44	27·53	33·10
Hydrogen c. c. initial	8·10	7·94	8·07	8·12	8·02	7·89
Hydrogen iodide c. c. formed	5·66	9·52	13·34	14·82	15·40	15·12

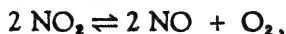
Calculate the amounts of hydrogen iodide to be expected from the law of mass action and compare them with those actually found.

Ans. 5·64; 9·49; 13·47; 14·93; 15·54; 15·40.

Problem 155. The variation in the density of nitrogen peroxide with change of temperature is given below :—

temperature	184°C.	279°C.	494°C.	620°C.
c. c. (N. T. P.)	143·5	116·6	58·6	19·6
weight in g	0·287	0·226	19·6	0·027.

If the dissociation takes place according to the equation

$$2\,NO_2 \rightleftharpoons 2\,NO + O_2,$$

calculate for each temperature the percentage of dissociation of nitrogen peroxide.

Ans. 5%; 12%; 59%; 98%.

Problem 156. At 49·7°C. and under a pressure of 93·75 mm., N_2O_4 is 77·8 per cent. dissociated into NO_2. At what pressure would the gas be 50% dissociated?

Ans. 431·1 mm.

Problem 157. In an experiment by Nernst and Wartenburg in which water vapour, oxygen and hydrogen were passed through a heated tube at 1207°C., the residual gases measured 0·6645 c. c. at (N. T. P.) and completely condensed to water, after exploding without leaving any residue. In addition to these gases, 1·66 c. c. of water was also collected. Calculate the percentage of dissociation of water.

Ans. 0·022 per cent.

Problem 158. At 14° the distribution coefficient of iodine between carbon tetrachloride and water is 79. A solution of iodine in tenth normal potassium iodide was shaken up with carbon tetrachloride. After equilibrium had been attained, 1 litre of the carbon tetrachloride phase contained 0·2022 gram molecule, whereas the same volume of the aqueous phase contained 0·02118 gram molecule of iodine. Calculate the equilibrium constant of the reaction $KI + I_2 \rightleftharpoons KI_3$.

Ans. $\frac{[KI]\,[I_2]}{[KI_3]} = 0{\cdot}000967.$

Problem 159. According to the measurements of Natausan at 21·5°, the degree of dissociation of N_2O_4 at 59·7 mm. pressure is 0·483, and at 617·6 mm. pressure, it is 0·174. Compare the values of K_p at the two pressures. Hence find the volume occupied by one molecule of N_2O_4 at 59·7 mm. pressure.

Ans. (1) $K_{59{\cdot}7} = 0{\cdot}1816$; (2) $K_{617{\cdot}6} = 0{\cdot}1972$; and (3) $V_{59{\cdot}7} = 422{\cdot}9$ litres.

Problem 160. The value of the equilibrium constant of the reaction between nitrogen and oxygen at a certain temperature is given by,

$$\frac{[NO]^2}{[N_2]\,[O_2]} = 4{\cdot}00 \times 10^{-4}.$$

Calculate approximately the yields of NO at this temperature and at atmospheric pressure given by a mixture of oxygen and

nitrogen where oxygen forms—10, 40, 70 and 80 per cent. by volume of the initial mixture. What mixture will give the maximum yield ?

Ans. (i) 0·58; (ii) 0·95; (iii) 0·90; (iv) 0·78.
The mixture containing 40% oxygen will give the maximum (about one per cent.) yield.

Problem 161. The partition coefficient of iodine for CS_2/water is 410. A solution of KI containing 8 grams per litre was shaken with CS_2 and iodine till equilibrium was established. The concentrations of iodine in aqueous and CS_2 layers, determined by titration with sodium thiosulphate, were found to be 2·15 grams and 35·42 grams per litre respectively. KI reacts with iodine in aqueous layer as $KI + I_2 = KI_3$. If KI and KI_3 are assumed to be insoluble in CS_2 and the concentration of the iodine in the aqueous layer, obtained by titration, is the sum of free iodine and the iodine combined with KI, calculate the dissociation constant of the tri-iodide expressing the concentrations in gram molecules per litre.

Ans. K = 0·001678.

Problem 162, At 1000° K, the degree of dissociation of steam is $3{\cdot}00 \times 10^{-5}$ per cent. Calculate the affinity of H_2 for O_2 at this temperature.

Ans. 45440 cals. / H_2O.

Problem 163. At 360°C. HI is dissociated to the extent of 20 per cent. Calculate the maximum amount of work obtainable at this temperature, when 2 g of H_2 and 254 g of gaseous I_2 yield 256 g of HI, both of the reactants being initially at unit concentration and the products being finally at unit concentration.

Ans. 3590 cals.

Problem 164. The dissociation pressure of the decahydrate of sodium sulphate at 15°C. is 7·9 mm. and the vapour pressure of water at the same temperature is 12·7 mm. Calculate the affinity of sodium sulphate for water.

Ans. 818·7 cals.

Problem 165. Examine the conditions for the formation of red lead from litharge, the following red lead dissociation pressures being given :—

Temperature °C	445°	500°	555°	636°
Dissociation pressure of oxygen	5 mm.	60 mm.	183 mm.	763 mm.

Ans. The maximum yield would be at about 520°C.

Problem 166. The equilibrium constant when hydrogen and iodine react at 445°C. (the B. P. of sulphur), is 50°C. Calculate the affinity between hydrogen and iodine at that temperature.

Ans. 5875 calories.

Problem 167. Dissociation pressure of calcium carbonate is 34·2 cms. at 840° K and 42 cms. at 860° K. Find its heat of dissociation between these temperatures.

Ans. − 31530 calories.

Problem 168. The dissociation pressure of $CaCO_3$ at 810°C. is 678 mm. and at 818°C., it is 760 mm. Calculate the affinity of CaO to CO_2 at atmospheric pressure at 810°C.

Ans. 246 cals.

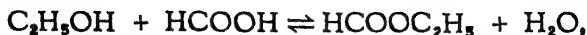
Problem 169. Determine the heat of reaction of

$$Fe + H_2O = FeO + H_2$$

given that the partial pressures of hydrogen and water vapour at equilibrium are respectively, 427 mm. and 333 mm. at 1025°C., and 450 mm. and 310 mm. at 900°C.

Ans. 3018 cals. per gram mol.

Problem 170. The heats of combustion of ethyl alcohol, formic acid and ethyl formate are 326·0 cals., 62·9 cals., and 391·7 cals. respectively. From this data, explain whether in the reaction

$$C_2H_5OH + HCOOH \rightleftharpoons HCOOC_2H_5 + H_2O,$$

the esterification would be helped by the elevation of temperature.

Ans. It will be retarded because though the sum of the heats of combustion of ethyl alcohol and formic acid is less than that of combustion of ethyl formate, by 2·8 cals., the heat of formation of water is far greater than this difference and the reaction is exothermic.

Problem 171. The ratios of the pressure of water vapour in equilibrium with $BaCl_2, 2H_2O$ (crystalline) to the pressure in equilibrium with pure water at the same temperature are 0·1905 at 18·5°C. and 0·3204 at 43·45°C. What is the heat of hydration of $BaCl_2$ per molecule of crystal formed ?

Ans. 3819 cals.

Problem 172. Calculate the approximate molecular heat of solution of aniline (C_6H_7N) in water, given the following data : 1 part by weight of aniline dissolves in 31·5 parts by weight of water at 12·5°C. and in 32·1 at 16°C.

Ans. 883·3 cals.

Problem 173. The theoretical density of N_2O_4 undissociated is 3·119 with respect to air as unity. The density falls to 2·65 at 26·7°C. and to 1·65 at 111·3°C. Calculate the heat of dissociation of the reaction $N_2O_4 \rightleftharpoons 2NO_2$.

($\log_e x = 2{\cdot}302 \log_{10} x$; the gas constant R = 2 calories.)

Ans. 12780 cals.

Problem 174. If the heat of an equilibrium reaction is 20,700 cals. per gram molecule at 27°C., calculate the percentage change in the equilibrium constant per one degree change of temperature.

Ans. – 10·87 % per degree rise in temperature.

Problem 175. Vapour pressure of benzene at 20°C. is 78 mm. while that at 30°C. is 118 mm. Find the latent heat of vaporisation of benzene.

Ans. – 8004 calories.

Problem 176. Calculate the heat of solution of succinic acid, given that the solubility of the acid at 0°C. and 8·5°C. is equal to 2·88 and 4·22 grams per 100 grams of water respectively.

Ans. − 6901 cals. per gram mol.

Problem 177. In the synthesis of nitric acid, the primary reaction is :

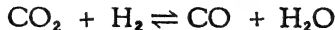
$$N_2 + O_2 = 2NO - 43200 \text{ cals.}$$

Assuming that the heat of the reaction is independent of the temperature, calculate the equilibrium constant at 2500° Abs., given that at 2000° Abs.

$$K = \frac{NO}{(N_2)^{\frac{1}{2}}(O_2)^{\frac{1}{2}}} = 0{\cdot}0153.$$

Ans. K, the equilibrium constant at 2500° Abs. = 0·04538.

Problem 178. At equilibrium the reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

is found to have − 10,500 cals. as the heat of reaction and K_p = 1·62 at 1273° Abs. Find the value of K_p at 973° Abs. and in the light of the result obtained, indicate which of the two temperatures you would choose for the industrial manufacture of hydrogen from water gas.

Ans. K_p at 973° Abs. = 0·4505.

The temperature of 973° Abs. is to be preferred. As the dissociation constant and consequently the amount of CO is greater at higher temperature, the concentration of hydrogen will therefore, be greater at the lower temperature.

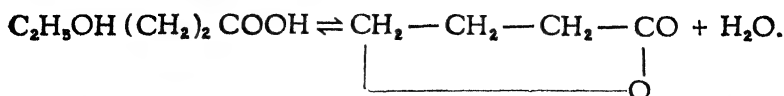
Problem 179. Diazoamido benzene ($C_6H_5N:N{\cdot}NHC_6H_5$) is converted into amidoazobenzene ($C_6H_5N:NC_6H_4NH_2$) under the the influence of aniline hydrochloride. The former compound liberates two-thirds of its nitrogen when boiled with dilute acids; the latter gives no nitrogen under these conditions. The progress of the reaction was therefore followed by with-

drawing from time to time a weighed portion of the reaction mixture and determining the volume of nitrogen evolved. From the following results of a series of measurements show that the reaction is monomolecular. The original mixture consisted of 0·6475 gram of aniline hydrochloride, 4·925 grams of diazoamido-benzene and 50 grams of aniline which acted as a solvent.

Time in hours.	Wt. of sample.	c. c. of moist N_2.	Barometric pressure.	Temperature.
18·11	2·645	22·8	750	14·0
66·25	5·255	21·8	748	12·5
115·20	5·940	12·9	753	8·5

Ans. As the values of the velocity constant (K = 0·01300; 0·01453; 0·01376 respectively) are nearly the same, the reaction is monomolecular.

Problem 180. The transformation of γ-hydroxy butyric acid into its lactone is a reversible action of the first order, as represented by the equation

$$C_2H_5OH\,(CH_2)_2\,COOH \rightleftharpoons \underbrace{CH_2 - CH_2 - CH_2 - CO}_{\text{ring closed through } O} + H_2O.$$

Assuming that only the acid is present in a solution at the commencement of the reaction, show that the course of the reaction will be represented by the formula :

$\dfrac{1}{t} \log \dfrac{A}{A - (1 + a)x}$ = constant, where A is the concentration of the acid at the commencement of the reaction, x is the amount of lactone formed after the time t and a the ratio of the concentrations of the lactone and acid when equilibrium is attained. Verify the formula for the following values of t and x, when A is 18·23 and a is 0·373.

t	80°	100°	160°
x	7·08	8·11	10·35.

Ans. constant = 0·00414; 0·00410; 0·00410.

Problem 181. In the reaction between equivalent quantities of potassium persulphate and hydrogen peroxide, the rate of decomposition of hydrogen peroxide was measured. The numbers given below represent c. c. of $\frac{N}{10}$ potassium permanganate equivalent to the peroxide remaining in solution. What is the order of the reaction ?

Time in hours	0	1	2·5	3·5	5	7
c. c. of $KMnO_4$	14·6	13·19	12·05	11·35	10·36	9·16

Ans. (1) Monomolecular ; (K = 0·06168, mean).

Problem 182. In the decomposition of hydrogen peroxide by colloidal platinum, the rate of decomposition of hydrogen peroxide was measured. The numbers given below represent c. c. of N/ 100 $KMnO_4$ solution equivalent to the peroxide remaining in solution :—

Time in min.	0	5	15	25	35
c. c. of $KMnO_4$ sol.	21·2	19·2	15·9	13·1	10·8

What is the order of the reaction? Calculate the velocity constants of the reaction.

Ans. (1) The reaction is unimolecular.

(2)

t	c. c. of $KMnO_4$	K
0	21·2	—
5	19·2	0·01975
15	15·9	0·01916
25	13·1	0·01925
35	10·8	0·01927

Problem 183. The decomposition of AsH_3 into solid arsenic and hydrogen can be followed by measuring from time to time the pressure of hydrogen (generated in the decomposition) at constant volume. In an experiment at 310°C. the pressures 'p' in mm., of mercury were obtained after the times 't' hours. Show from these figures that the reaction is of the first order.

t in hours	0	5·5	6·5	8
p in mm.	733·32	805·78	818·11	835·34

Ans. As the values of the velocity constant differ very little, from the average value (0·04037), the reaction is of the first order.

Problem 184. When electrolytic gas was circulated over porcelain heated to 450°C. the following observations were made of the pressure of the gas remaining (dry) at intervals of 24 hours :—

Time in days	0	1	2	3	4	5
Pressure in mm.	465	232	116	58	29	14·5

What information do these figures afford as to the order of the change occurring?

Ans. The pressures indicate the reaction to be unimolecular, but, since it takes place on the surface of the porcelain, no definite conclusion can be made as regards the order of the reaction.

Problem 185. In an investigation of the reaction between hydrogen peroxide and hydriodic acid, the following results were obtained :—

Experiment.	Concentration of HI.	Concentration of H_2O_2.
I	0·02	0·02
II	0·01	0·01
III	0·005	0·005

The time taken for the completion of one-fourth of the reaction was respectively 21·7, 43·2, and 97·4 minutes. What is the order of the reaction ?

Ans. Bimolecular.

Problem 186. The concentrations of a compound undergoing complete change were, 5·72, 3·23 and 1·96 at the times 10, 30, and 60 hours from the commencement of the reaction.

Ascertain the apparent order of the reaction, the probable initial concentration of the compound, and the velocity constant.

Ans. (1) Bimolecular ; (2) Initial concentration (mean) = 9·26. (3) Velocity constant (mean) = 0·00670.

Problem 187. The rate of reaction between iodine and potassium phenylpropiolate in equivalent quantities was determined by measuring the rate of disappearance of the iodine. 25 c. c. of the solution were withdrawn after suitable intervals from the reaction-mixture and titrated with N/10 sodium thiosulphate. The following figures were obtained :—

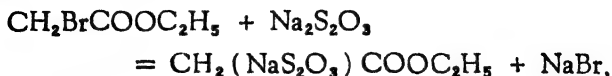
Time in hours	0	20	24	28	42
Titration	24·96	10·39	9·25	8·45	6·36 c. c.

What is the order of the reaction, and what is the velocity constant?

Ans. (1) The reaction is bimolecular

(2) K, the velocity constant is 0·002805 (mean value).

Problem 188. In an experiment on the rate of reaction between sodium thiosulphate and ethyl brom acetate which react according to the equation, :—

$$CH_2BrCOOC_2H_5 + Na_2S_2O_3 = CH_2(NaS_2O_3)COOC_2H_5 + NaBr,$$

50 c. c. of the reaction mixture required the following amounts of 0·0110 N iodine at the corresponding times from the commencement of the reaction :—

t in min.	0	5	10	25	40	∞
c. c. of iodine sol.	37·25	24·70	18·75	11·60	8·85	4·40

Show that the reaction is of the second order and calculate the value of the velocity constant, expressing the concentrations in gram equivalents per litre.

Ans. K = 0·2902 (average).

Problem 189. Daniel and Johnston obtained the following results for the velocity constant of the reaction $N_2O_5 \rightleftharpoons N_2O_4 + \frac{1}{2}O_2$:—

Temperature	45°	25°	0°
K	0·0299	0·00203	0·0000472

In calculating K, the times were expressed in minutes. Calculate the heat of activation from these results.

Ans. (1) 22940 cals. (between 45 and 25)

(2) 24320 cals. (between 25 and 0).

Problem 190. From the following values obtained for the velocity coefficient of the decomposition of N_2O_5, find the energy of activation.

t°C.	45°	35°	25°
$K \times 10^4$	4·95	1·35	0·338

Ans. 25290 cals. between 45 and 35

25250 ,, ,, 35 ,, 25.

CHAPTER V

ELECTROCHEMISTRY

28. **Transport Number.**— The transport number of an ion is the fraction of the electricity that flows through the electrolyte. It is usually determined by observing the fall in the concentration (either, near the cathode or near the anode) and the total electrolyte decomposed by the current during the given time. The transport number of the anion is called n.

$$n = \frac{\text{fall in concentration at cathode}}{\text{amount of the electrolyte decomposed by the current}} .$$

The transport number of the cation is called $(1 - n)$.

$$(1 - n) = \frac{\text{fall in concentration at anode}}{\text{amount of the electrolyte decomposed by the current}} .$$

The manner in which the concentration changes in the cathode and the anode regions will be understood by considering the stages occurring during the electrolysis :

Stage I represents the condition of the dissolved electrolyte before closing the current.

Cathode			Anode
	+ + + + +	+ + + + +	+ + + + +
Stage I	− − − − −	− − − − −	− − − − −
	Cathode compartment		Anode compartment

Let us assume that each compartment contains five pairs* of ions, the concentration being uniform throughout the solution.

* The number of ions in each compartment is very great but the calculation adopted in considering the relative fall in the anode and the cathode compartments will not be affected by this great number.

Stage II. When the circuit is closed, the ions are set in motion; the positive ions (cations) move towards cathode, and the negative ions (anions) towards the anode. If the mobilities of cations and anions are in the ratio of 2 : 3, during the time two cations leave the anode compartment and migrate towards the cathode, three anions leave the cathode compartment and go towards the anode. The cathode compartment will be poorer by three anions, while the anode compartment will be poorer by two cations. The distribution of ions at the end of the period and before any discharge occurs will be as represented below :—

Cathode — Anode

	+ + + + + + +	+ + + + +	+ + +
Stage II	– –	– – – – –	– – – – – – – –
	Cathode compartment		Anode compartment

Stage III. There are five ions in each compartment which have no partners and they get discharged at the electrodes and the distribution of ions after the discharge will be as represented below :—

Cathode — Anode

	+ +	+ + + + +	+ + +
Stage III	– –	– – – – –	– – –
	Cathode compartment		Anode compartment

It is assumed that no secondary reactions occur at the cathode or at the anode. It will be obsebrved that :

(1) The total number of ions discharged, at the cathode and at the anode is five. This is the result of the total quantity of electricity that flowed through the solution in the given time.

(2) The fall in concentration round the cathode is proportional to the mobility (migration velocity) of anions.

(3) And the fall in concentration round the anode is proportional to the mobility (migration velocity) of cations.

(4) The concentration of the middle compartment is not affected.

In electrolysis, secondary reactions however often occur; the products discharged at the electrodes may decompose if they are unstable or they may react with the electrodes or with water. When the metal of the electrode is acted on by the anions, the concentration in that compartment is increased as represented below :—

Cathode		Anode
+ +	+ + + + +	+ + + + + + + +
– –	– – – – –	– – – – – – – –
Cathode compartment		Anode compartment

In calculating the transport number, correction for such an increase in concentration in the anode compartment must be made. Thus in the above illustration, this amount is five, produced by the action of the discharged ions on the anode. From the actual concentration as determined by analysis (eight) substract (five) the initial concentration. Then three (8 – 5) will represent the concentration (near the anode) which would have been observed, had there been no secondary reaction.

29. **Views of Nernst about of the origin of E. M. F.** and E. M. F. produced when a metal is immersed in pure water or in a solution of its salt.

When a substance (*e.g.* NaCl) is added to water it continues to dissolve till a saturated solution is formed. In a saturated

solution, the solid and the dissolved part are indynamic equilibrium. The solid still continues to dissolve while the dissolved part passes back into the solid condition. But in the saturated solution the velocities of the two processes being equal, no change in the concentration occurs. The tendency of the solid to dissolve is called its *solution pressure* and depends on the nature of the solid. The tendency of the dissolved body to pass back into the solid condition depends on the osmotic pressure of the solution.

Nernst extended this idea to the solution of metals in pure water or in solutions of their salts. He assumed that each metal has a characteristic *solution pressure* which measures the tendency of the metal to pass into solution. A metal, however, passes into the solution as charged particles or ions while the osmotic pressure of the ions causes the ions to deposit themselves on the metal as discharged metallic particles. When a metal passes into solution as a positively charged ion, the metal becomes negatively charged and an electric double layer is formed at the surface of the metal, and inspite of the difference in the solution pressure of the metal and the osmotic pressure of ions, solution of the metal does not continue till this electric double layer is destroyed. The E. M. F. between the metal and the surrounding layer of ions (which opposes solution) can be measured, by the work done to equalise this difference between the solution pressure of the metal and the osmotic pressure of the solution in which the metal is immersed.

The work done when a gram molecule of a gas changes from a pressure P to a pressure p, is $2{\cdot}303\ RT \log \frac{P}{p}$. Suppose Ag is immersed in a solution of its salt, and assume that the passage of metal particles into the solution follows the gas laws. As Ag particles pass from a solution pressure P to a pressure p, which is the osmotic pressure of the Ag ions in the solution, the work done during the change is $2{\cdot}303\ RT \log \frac{P}{p}$. But the solution of silver can occur only when the electrical double layer is eliminated. The electric work done, when a gram atom of silver changes into Ag ions, is EnF where

E = E. M. F. in volts, n = valency of the metal, and

F = a Faraday, *i. e.*, charge carried by a mono-valent gram atom in the form of ion.

The electrical work is also equal to the work done when a gram atom of Ag passes from a pressure P to a pressure p.

$$\therefore \quad EnF = 2{\cdot}303 \; RT \log \frac{P}{p}$$

$$\text{or,} \quad E = \frac{2{\cdot}303 \; RT}{nF} \log \frac{P}{p}.$$

To obtain E in volts, R must be expressed in volt-coulomb-units. (R = 8·317 volts-coulombs.)

For a temperature of 18°C.,

$$E = \frac{2{\cdot}303 \times 8{\cdot}317 \times 291}{n \times 96540} \log \frac{P}{p};$$

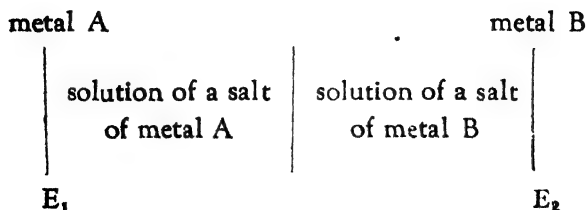
$$\textit{i. e.} \quad E = \frac{0{\cdot}0577}{n} \log \frac{P}{p}.$$

and for a temperature of 25°C.,

$$E = \frac{0{\cdot}0591}{n} \log \frac{P}{p}.$$

As pressure is proportional to concentration in dilute solutions, instead of the pressures P and p, the concentrations C and c can be used. Then, for ordinary temperatures,

$$E = \frac{0{\cdot}058}{n} \log \frac{C}{c}.$$

The E. M. F. of a cell of the form :

is $E = E_1 - E_2 = \frac{0.058}{n} \left\{ \log \frac{C_1}{c_1} - \log \frac{C_2}{c_2} \right\}$,

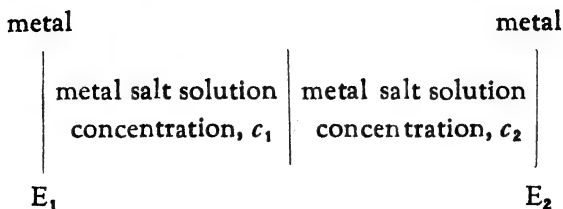
where

$$E_1 = \text{electrode potential of the metal A} = \frac{0.058}{n} \log \frac{C_1}{c_1}.$$

$$E_2 = \text{electrode potential of the metal B} = \frac{0.058}{n} \log \frac{C_2}{c_2}.$$

It is assumed that both the metals have the same valency.

30. **The E. M. F. of a Concentration Cell.**— The E. M. F. of a concentration cell (E) of the form

metal		metal
metal salt solution concentration, c_1	metal salt solution concentration, c_2	
E_1		E_2

is $E = E_1 - E_2$.

In this equation the difference in potential at the junction of the two solutions is neglected.*

$$\therefore \quad E_1 = \frac{0.058}{n} \log \frac{C}{c_1}$$

$$E_2 = \frac{0.058}{n} \log \frac{C}{c_2}$$

$$E_1 - E_2 = \frac{0.058}{n} \left\{ \log \frac{C}{c_1} - \log \frac{C}{c_2} \right\}$$

$$E = \frac{0.058}{n} \log \frac{c_2}{c_1}$$

Normal potential when the electrode passes into the solution as a positive ion can be calculated by using the formula :

* The potential difference at the junction of the two solutions is generally eliminated by interposing a solution of a salt, (1) which does not react with the solutions of the salts of the metal or metals, *e. g.* KCl or NH_4NO_3, or (2) the migration velocities of whose ions are approximately equal.

$$E = 0{\cdot}058 \log \frac{P}{p} .$$

Since $p = 1$,

$$E = 0{\cdot}058 \left(\log P - \log 1 \right)$$
$$= 0{\cdot}058 \log P$$
$$= e_n .$$

e_n is called the normal potential. e for concentration c is $0{\cdot}058 \log \frac{P}{c} = 0{\cdot}058 \log P - 0{\cdot}058 \log c$

$$= e_n - 0{\cdot}058 \log c.$$

Here the electrode is negative.

For an electrode like Cl_2 which pass into solution as negative ions, the electrode is positive and ions are negative.

$$\therefore e = e_n + 0{\cdot}058 \log c.$$

The E. M. F. at a given temperature can be calculated, when heat of the reaction (Q) and the temperature coefficient of E. M. F. $\left(\frac{dE}{dT} \right)$ is known, by the application of Gibbs Helmholtz's equation

$$A - Q = T. \frac{dA}{dT} .$$

Since $A = EnF$,

$$E = \frac{Q}{nF} + T \cdot \frac{dE}{dT} .$$

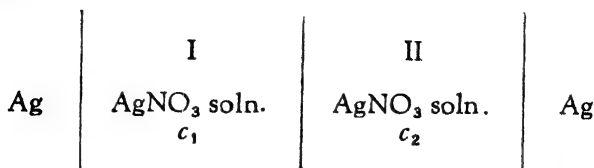
The E. M. F. measurements are specially useful in determining :—

(1) The solubility of sparingly soluble salts.

(2) The valency of the ions.

(3) The hydrolysis of salts.

31. **The E. M. F. of the Liquid-Liquid Junction** in solutions which contain the same univalent ions in different concentrations. Let us consider the following concentration cell where $c_1 > c_2$.

Ag	I $AgNO_3$ soln. c_1	II $AgNO_3$ soln. c_2	Ag

When a gram ion is discharged at the electrodes, the total E. M. F. can be calculated from the amount of the ions that migrate :—

(i) $\frac{u}{u+v}$ equivalents of Ag ions migrate from II to I, while one equivalent of Ag ions is discharged at the electrode in I, which becomes poorer in Ag ions by $1 - \frac{u}{u+v}$ or $\frac{v}{u+v}$ equivalents; while that in II becomes richer in Ag ions by $\left(1 - \frac{u}{u+v}\right)$ or $\frac{v}{u+v}$ equivalents.

(ii) $\frac{v}{u+v}$ equivalents of NO_3 ions migrate from I to II, the solution in I becomes poorer in NO_3 ions by $\frac{v}{u+v}$ NO_3 ions and that in II becomes richer by $\frac{v}{u+v}$ NO_3 ions.

The net result in the working of the cell is thus the transfer from the stronger to the weaker solution, of $\frac{v}{u+v}$ Ag ions and $\frac{v}{u+v}$ NO_3 ions from I to II.

The work done in electrical terms is :

$$E_1 F = \frac{2v}{u+v} RT \log_e \frac{c_1}{c_2} .$$

The total E. M. F., E_1 produced is

$$E_1 = \frac{2v}{u + v} \cdot \frac{RT}{F} \log_e \frac{c_1}{c_2} .$$

If the electrode processes are only taken into consideration

$$EF = RT \log_e \frac{c_1}{c_2} ,$$

$$\therefore \quad E = \frac{RT}{F} \log_e \frac{c_1}{c_2} .$$

Since the ions are univalent, $F = 1$

$$\therefore \quad E_1 = \frac{2v}{u + v} \cdot RT \log_e \frac{c_1}{c_2} \text{ and } E = RT \log_e \frac{c_1}{c_2} .$$

The total E. M. F. is equal to E_1 (E. M. F. due to the liquid junction potential difference) minus E (E. M. F. due to the electrode processes).

$$\therefore \quad E_1 - E = \frac{2v}{u + v} \cdot RT \log_e \frac{c_1}{c_2} - RT \log_e \frac{c_1}{c_2}$$

$$= \left\{ \frac{2v}{u + v} - 1 \right\} RT \log_e \frac{c_1}{c_2}$$

$$= \left\{ \frac{2v}{u + v} - \frac{u + v}{u + v} \right\} RT \log_e \frac{c_1}{c_2}$$

$$= - \frac{u - v}{u + v} RT \log_e \frac{c_1}{c_2} .$$

The negative sign shows that the anode becomes more negative by this amount. The potential difference is taken in the same direction as the E. M. F. of the cell, when the liquid junction potential difference is neglected. It will be thus evident that E is increased if v is greater than u as in the cell considered above; while E is decreased if v is less than u as in a cell, where the electrolyte is ' HCl ' solution of different concentrations.

Problems with Solutions

Problem 191. The same current is passed through acidulated water and a solution of stannous chloride. What volume of detonating gas (mixture of H_2 and O_2) measured at 0°C. and 760 mm. pressure is evolved from the water when one gram of tin is deposited from the other solution?

Solution :

Tin (Sn-ous)	2H	O
119	2	16
1	$\frac{2 \times 1}{119}$	$\frac{16}{119}$

The volume of $\frac{2}{119}$ g of H_2 at 0°C. and 760 mm. will be

$$\frac{22400 \times 2}{119 \times 2} = 188{\cdot}2 \text{ c. c.}$$

and that of $\frac{16}{119}$ g of O_2 under the same conditions

$$\frac{22400 \times 16}{119 \times 32} = 94{\cdot}1 \text{ c. c.}$$

The total volume of the detonating mixture is, therefore,

$$= (188{\cdot}2 + 94{\cdot}1 =)\ 282{\cdot}3 \text{ c. c.}$$

Ans. The volume of the detonating mixture is 282·3 c. c.

Problem 192. The same current was passed through the aqueous solutions of copper sulphate and silver nitrate. Calculate the quantity of silver deposited if 5·38 g of copper sulphate were decomposed by the current.

Solution :

$CuSO_4, 5H_2O$	2 Ag
249·5	216

$$\text{The silver deposited} = \frac{216 \times 5{\cdot}38}{249{\cdot}5}$$

$$= 4{\cdot}658$$

Ans. The amount of silver deposited is 4·658 g.

Problem 193. A conductivity cell has horizontal circular platinum electrodes of radius 0·77 cm. and the distance between them is 1·43 cm. The cell is filled with $\frac{N}{20}$ sodium nitrate solution and it is found that a potential difference of 0·61 volts produces a current of $3{\cdot}13 \times 10^{-3}$ ampere in the cell. Calculate the specific and equivalent conductivity of the solution.

Solution :

$$R = \frac{E}{C}$$

$$= \frac{0{\cdot}61}{3{\cdot}13 \times 10^{-3}}.$$

As the resistance is directly proportional to the length and inversely proportional to the cross section,

$$\text{the specific resistance} = \frac{0{\cdot}61 \times 3{\cdot}14 \times 0{\cdot}77 \times 0{\cdot}77}{3{\cdot}13 \times 10^{-3} \times 1{\cdot}43}$$

$$\therefore \quad \text{The specific conductivity} = \frac{3{\cdot}13 \times 10^{-3} \times 1{\cdot}43}{0{\cdot}61 \times 3{\cdot}14 \times 0{\cdot}77 \times 0{\cdot}77}$$

$$= 3{\cdot}941 \times 10^{-3}.$$

$$\text{The equivalent conductivity} = 20000 \times 3{\cdot}941 \times 10^{-3}$$

$$= 78{\cdot}820.$$

Ans. (*a*) Specific conductivity, $3{\cdot}941 \times 10^{-3}$
(*b*) Equivalent conductivity, 78·820.

Problem 194. The resistance of 0·1N solution of KCl in a conductivity cell is found to be 76·52 ohms and that of 0·04N solution of $AgNO_3$ to be 211·4 ohms. If the specific conductivity of KCl solution is $11{\cdot}2 \times 10^{-3}$ r. o., calculate the equivalent conductivity of $AgNO_3$ solution.

Solution : The cell constant C is given by the equation

$$C = RK,$$

where, R is the resistance and K the specific conductivity. Hence from the data of KCl soln.,

$$C = 76{\cdot}52 \times 11{\cdot}2 \times 10^{-3}.$$

If K_1 is the specific conductivity of $AgNO_3$ solution,

$$C = 211{\cdot}4 \times K_1.$$

Then, $211{\cdot}4\ K_1 = 76{\cdot}52 \times 11{\cdot}2 \times 10^{-3}$.

$$\therefore \quad K_1 = \frac{76{\cdot}52 \times 11{\cdot}2 \times 10^{-3}}{211{\cdot}4}.$$

$\therefore \quad \Lambda = \dfrac{K_1\,1000}{c}$, where the equivalent conductivity $= \Lambda$

$$= \frac{76{\cdot}52 \times 11{\cdot}2 \times 10^{-3} \times 1000}{211{\cdot}4 \times 0{\cdot}04}$$

$$= 101{\cdot}4.$$

Ans. The equivalent conductivity of 0·04N $AgNO_3$ solution is 101·4 r. o.

Problem 195. The specific conductivity of a solution containing 0·167 gram equivalent of acetic acid per litre is $5{\cdot}84 \times 10^{-4}$ r. o. If the ionic conductivity of $H^{\cdot}$ and CH_3COO' ions are respectively 318 and 32 r. o., calculate (i) the degree of dissociation, and (ii) the $H^{\cdot}$ ion concentration and (iii) the dissociation constant of the acid.

Solution : Equivalent conductivity, $\Lambda = K \times 1000\,V$

$$= \frac{K}{c}\,1000.$$

$$\therefore \quad \Lambda = \frac{5{\cdot}84 \times 10^{-4} \times 1000}{0{\cdot}167}$$

$$= 3{\cdot}497 \text{ r. o.}$$

The equivalent conductivity at infinite dilution,

$$\Lambda_\infty = 318 + 32$$

$$= 350 \text{ r. o.}$$

(i) The degree of dissociation,

$$\alpha = \frac{\Lambda}{\Lambda_\infty}$$

$$= \frac{3{\cdot}497}{350}$$

$$= 0{\cdot}009991.$$

(ii) The $H^{\cdot}$ ion concentration $= 0{\cdot}009991 \times 0{\cdot}167.$

$= 0{\cdot}001668$

or, expressed as pH $= 2{\cdot}7777.$

(iii) The dissociation constant, $K = \dfrac{(\alpha c)^2}{(1 - \alpha)c}$

i. e., $$\frac{(0{\cdot}009991 \times 0{\cdot}167)^2}{(1 - 0{\cdot}009991) \times 0{\cdot}167} = 1{\cdot}68 \times 10^{-5}.$$

Ans. (i) 0·009991, the degree of dissociation.

(ii) 0·001668, the $H^{\cdot}$ ion concentration.

(iii) $1{\cdot}68 \times 10^{-5}$, the dissociation constant.

Problem 196. Given that the dissociation constant of acetic acid at 25°C. is $1{\cdot}8 \times 10^{-5}$, find the pH value of (*a*) a solution containing 0·185 g mol of acetic acid and 0·015 g mol of sodium acetate per litre, and (*b*) a solution containing 0·019 g mol of acetic acid, and 0·181 g mol of sodium acetate per litre

Solution : (*a*) It is assumed that sodium acetate is completely dissociated. If x be the degree of dissociation of acetic acid in the presence of sodium acetate, the concentration, (i) of $[H^{\cdot}] = 0{\cdot}185x$, and (ii) of $[CH_3COO'] = 0{\cdot}185x + 0{\cdot}015.$

$$\frac{[H^{\cdot}]\,[CH_3COO']}{[CH_3COOH]} = \frac{0{\cdot}185x\,(0{\cdot}185x + 0{\cdot}015)}{(1 - x) \times 0{\cdot}185} = 1{\cdot}8 \times 10^{-5}.$$

As x is very small compared to 1, $1 - x$ becomes 1 and $0{\cdot}185x + 0{\cdot}015$ becomes 0·015. The above equation then reduces to

$$\frac{0{\cdot}185x \times 0{\cdot}015}{0{\cdot}185} = 1{\cdot}8 \times 10^{-5}.$$

$$\therefore \quad 0{\cdot}015x = 1{\cdot}8 \times 10^{-5}$$

$$x = \frac{1{\cdot}8 \times 10^{-5}}{0{\cdot}015}$$

$$= 1{\cdot}2 \times 10^{-3}.$$

The $H^{\bullet}$ ion concentration $= 0{\cdot}185 \times 1{\cdot}2 \times 10^{-3}$ gram ion / *l.*

$= 0{\cdot}2220 \times 10^{-3}$

$= 2{\cdot}220 \times 10^{-4}$

$\log [H^{\bullet}] = \bar{4}{\cdot}3464$

$= -3{\cdot}6536.$

$\therefore \; pH = 3{\cdot}6536$

(*b*) Similarly,

$$\frac{0{\cdot}019x\,[0{\cdot}019x + 0{\cdot}181]}{(1 - x)\,0{\cdot}019} = 1{\cdot}8 \times 10^{-5}.$$

Simplifying as in (*a*), one gets

$0{\cdot}181x = 1{\cdot}8 \times 10^{-5}.$

$\therefore \; x = 9{\cdot}945 \times 10^{-5}$

$[H^{\bullet}] = 9{\cdot}945 \times 10^{-5} \times 0{\cdot}019$

$= 0{\cdot}189 \times 10^{-5}$

$\log [H^{\bullet}] = \bar{6}{\cdot}2764$

$pH = 5{\cdot}7236$

Ans. (*a*) pH, 3·6536 and (*b*) pH, 5·7236.

Problem 197. In order to ascertain whether a process for the electrolytic deposition of copper was economical, an electrolytic cell was placed in series with a voltameter. One gram of copper was deposited in the cell while 723 c. c. of moist hydrogen at 14°C. and 765 mm. Hg pressure was collected in the voltameter. (Tension of water at 14°C. = 11·9 mm.) What is the current efficiency?

***Solution*:** Find the number of molecules (M) of H_2 liberated.

Pressure of dry Hydrogen $= 765 - 11{\cdot}9 = 753{\cdot}1.$

$$PV = nRT.$$

$$\frac{753{\cdot}1 \times 0{\cdot}723}{760} = n \times 0{\cdot}08204 \times 287$$

$$\therefore \quad n = \frac{753{\cdot}1 \times 0{\cdot}723}{760 \times 0{\cdot}08204 \times 287}$$

$$= 0{\cdot}03043.$$

Amount of Cu to be theoretically liberated

$$= \frac{63{\cdot}57 \times 0{\cdot}03043 \times 2{\cdot}016}{2{\cdot}016}$$

$$= 1{\cdot}932$$

$$\text{Efficiency} = \frac{1}{1{\cdot}932} = 0{\cdot}5175 \text{ or } 51{\cdot}75\%.$$

Ans. Efficiency 51·75%.

Problem 198. If the dissociation constant of propionic acid is $1{\cdot}3 \times 10^{-5}$ at 25°C., find the concentration of the solution having $[H^{\cdot}] = 5 \times 10^{-3}$.

Solution: $C_2H_5COOH = C_2H_5COO' + H^{\cdot}$.

$$\frac{[C_2H_5COO'][H^{\cdot}]}{[C_2H_5COOH]} = K.$$

If $[H^{\cdot}] = 5 \times 10^{-3}$, then $[C_2H_5COO']$ must have the same value. Then if c be the required concentration in g mol per litre,

$$\frac{(5 \times 10^{-3})^2}{(c - 5 \times 10^{-3})} = 1{\cdot}3 \times 10^{-5}$$

5×10^{-3} being very small compared to c, $c - 5 \times 10^{-3}$ can be taken as c only. Then,

$$\frac{(5 \times 10^{-3})^2}{c} = 1{\cdot}3 \times 10^{-5}$$

$$\therefore \quad c = \frac{2{\cdot}5 \times 10^{-5}}{1{\cdot}3 \times 10^{-5}}$$

$$= 1{\cdot}923 \text{ mol}/l.$$

Ans. The required concentration is 1·923 mol/*l*.

Problem 199. A solution containing 0·0847 g of $AgNO_3$ in 10·058 g of solution was electrolysed between silver electrodes. After electrolysis 27·04 g of the anode solution was found to contain 0·2818 g of $AgNO_3$. In a silver voltameter in series with the electrolytic cell, 0·06588 g of silver was deposited. Calculate the transport number of $Ag^{\bullet}$ and NO_3' ions.

Solution : The total quantity of electricity passed through the solution is $\dfrac{0{\cdot}06588 \times 96540}{108}$.

The amount of Ag in 27·04 g of the solution in the beginning is $\dfrac{0{\cdot}0847 \times 27{\cdot}04 \times 108}{10{\cdot}058 \times 170} = 0{\cdot}1446$ g.

The amount of Ag in 27·04 g of the anode solution after electrolysis is $\dfrac{0{\cdot}2818 \times 108}{170} = 0{\cdot}1790$ g.

This increase is due to the amount of Ag dissolved by NO_3' from the silver anode. The amount so dissolved will be the same as deposited in the voltameter. Had there been no secondary reaction ($Ag + NO_3' \rightarrow Ag^{\bullet} + NO_3'$) the amount would have been $0{\cdot}1790 - 0{\cdot}06588 = 0{\cdot}1131$ and the fall in concentration, $0{\cdot}1446 - 0{\cdot}1131 = 0{\cdot}0315$.

The transport number of $Ag^{\bullet}$ ions

$$= \frac{\text{Fall (in gm equivalent) round the anode}}{\text{Total amount of electricity passed}}$$

$$= \frac{0{\cdot}0315 \times 96540}{108} \div \frac{0{\cdot}06588 \times 96540}{108}$$

$$= \frac{0{\cdot}0315}{0{\cdot}06588}$$

$$= 0{\cdot}4779.$$

The transport number of NO_3' ions $= 1 - 0{\cdot}4779 = 0{\cdot}5221$.

Ans. (1) Transport number of $Ag^{\bullet}$ ions is 0·4779

(2) Transport number of NO_3' ions is 0·5221.

Problem 200. At a given temperature a litre of a saturated solution of silver bromate contains, S = 0·0081 gram mol of the salt. c = 0·0085 gram mol of $AgNO_3$ is then added. Calculate the new solubility S″ of silver bromate, assuming that both the salts are practically completely dissociated in the solution.

Solution :

The solubility product of silver bromate = $(0{\cdot}0081)^2$

Let x be the gram equivalent of $Ag^{\cdot}$ and BrO_3' in a litre after addition of 0·0085 gram mol $AgNO_3$. Then,

$$(0{\cdot}0085 + x)(x) = (0{\cdot}0081)^2$$

$$x^2 + 0{\cdot}0085x = (0{\cdot}0081)^2$$

$$x^2 + 0{\cdot}0085x + (0{\cdot}00425)^2 = (0{\cdot}0081)^2 + (0{\cdot}00425)^2$$

$$(x + 0{\cdot}00425)^2 = 83{\cdot}67 \times 10^{-6}$$

$$(x + 0{\cdot}00425)^2 = (9{\cdot}147 \times 10^{-3})^2.$$

$$\therefore \quad (x + 0{\cdot}00425)^2 - (9{\cdot}147 \times 10^{-3})^2 = 0$$

$$(x + 0{\cdot}00425 - 0{\cdot}009147) = 0.$$

$$\therefore \quad x = 0{\cdot}009147 - 0\ 004250$$

$$= 0{\cdot}004897.$$

Ans. The solubility S″ of $AgBrO_3$ is 0·004897 gram mol / ***l.***

Problem 201. At 25°C. the E. M. F. of the cell

Ag | 0·1N $AgNO_3$ | saturated NH_4NO_3 | 0·1N calomel electrode is 0·396 volts and that of the cell

Ag | saturated solution of Ag ($C_2H_3O_2$) | saturated NH_4NO_3 | 0·1N calomel electrode

is 0·383 volts. If 0·1N $AgNO_3$ is 82% dissociated, calculate (a) the $Ag^{\cdot}$ ion concentration in the saturated solution of silver acetate and (b) the degree of dissociation of the saturated solution, given that the solubility of the silver acetate at 25°C. is 0·0664 gram molecule per litre.

Solution :

Let c_0 be the concentration of the metal ion in calomel.

c_1 ,, ,, ,, ,, ,, ,, ,, ,, 0·1N $AgNO_3$

c_2 ,, ,, ,, ,, ,, ,, ,, ,, Ag acetate.

and E_1 the E. M. F. of Ag | 0·1N $AgNO_3$ cell.

and E_2 ,, ,, ,, Ag | Saturated Ag acetate ,,

Then, $$E_1 = \frac{0·058}{n} \log \frac{c_1}{c_0} \quad \ldots \quad \ldots \quad \ldots \quad A$$

$$E_2 = \frac{0·058}{n} \log \frac{c_2}{c_0} \quad \ldots \quad \ldots \quad \ldots \quad B$$

Subtract B from A :

$$E_1 - E_2 = \frac{0·058}{n} (\log c_1 - \log c_0 - \log c_2 + \log c_0).$$

Substituting the values ($n = 1$) :

$$0·396 - 0·383 = 0·058 (\log 0·082 - \log c_2)$$

$$\frac{0·013}{0·058} = \bar{2}·9138 - \log c_2$$

$$0·2241 = -1·0862 - \log c_2$$

$$1·3103 = -\log c_2$$

$$-1·3103 = \log c_2$$

$$\bar{2}·6897 = \log c_2$$

$$\therefore \quad c_2 = 0·04894 \text{ concentration of } Ag^{\cdot}.$$

Ans. (a) The concentration of $Ag^{\cdot}$ is 0·04894.

(b) The degree of dissociation $= \frac{0·04894}{0·06640} = 0·7375.$

Problem 202. In a saturated solution of sulphuretted hydrogen, $[H^{\cdot}]^2 \times [S'']= 1·1 \times 10^{-23}$ is stated to hold. Assuming that a dilute solution of hydrochloric acid is completely ionised and that the solubility product of ferrous sulphide is $1·5 \times 10^{-19}$, calculate the minimum concentration of hydro-

gen chloride required to prevent the precipitation of ferrous sulphide from a solution containing 0·112 g $Fe^{\cdot\cdot}$ per litre.

Solution : Ionic concentration of Fe $= \frac{0{\cdot}112}{56} = 2 \times 10^{-3}$.

Concentration of sulphur ion in ferrous sulphide solution is

$$= \frac{1{\cdot}5 \times 10^{-19}}{0{\cdot}002}$$

$$= 0{\cdot}75 \times 10^{-16}$$

$$= 7{\cdot}5 \times 10^{-17} \qquad (\text{conc. of } S'')$$

Concentration of $H^{\cdot}$ ion in H_2S solution

$$[H^{\cdot}]^2 = \frac{1{\cdot}1 \times 10^{-23}}{7{\cdot}5 \times 10^{-17}}$$

$$= 0{\cdot}1467 \times 10^{-6}$$

$$= 14{\cdot}67 \times 10^{-8}.$$

$$\therefore \quad [H^{\cdot}] = 3{\cdot}83 \times 10^{-4}.$$

$$\therefore \quad [HCl] = 3{\cdot}83 \times 10^{-4}$$

Ans. The minimum concentration of HCl required is $3{\cdot}83 \times 10^{-4}$ gram mols / litre.

Problem 203. The specific conductivity of a saturated solution of silver bromide is $0{\cdot}057 \times 10^{-6}$ reciprocal ohms, after allowing for the conductivity of water. If the ionic conductivities of the silver and bromide ions are 56·3 and 69·5 respectively, calculate the solubility of silver bromide.

Solution : It is assumed that AgBr is at this dilution completely dissociated, so that the equivalent conductivity at this dilution is equal to the equivalent conductivity at infinite dilution.

$$\therefore \quad \Lambda = \Lambda_{\infty}$$

$$\Lambda_{\infty} = 56{\cdot}3 + 69{\cdot}5$$

$$= 125{\cdot}8$$

$$\Lambda = \frac{1000\ K}{c}$$

where K is the specific conductivity and c the concentration in gram equivalent per litre.

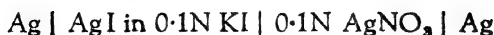
$$\therefore \quad 125{\cdot}8 = \frac{1000 \times 0{\cdot}057 \times 10^{-6}}{c}$$

$$\therefore \quad c = \frac{1000 \times 0{\cdot}057 \times 10^{-6}}{125{\cdot}8}$$

$$= 4{\cdot}531 \times 10^{-7} \text{ gram equivalent per litre.}$$

Ans. $8{\cdot}519 \times 10^{-5}$ grams per litre.

Problem 204. The E. M. F. of the cell

Ag | AgI in 0·1N KI | 0·1N $AgNO_3$ | Ag

is − 0 814 volts at 18°. Assuming that KI and $AgNO_3$ are completely dissociated, calculate the solubility of AgI at 18°.

Solution :

$$E = \frac{0{\cdot}058}{n} \log \frac{c_1}{c_2}$$

$$-0{\cdot}814 = 0{\cdot}058 \log \frac{c_1}{0{\cdot}1}$$

$$-\frac{0{\cdot}814}{0{\cdot}058} + \log 0{\cdot}1 = \log c_1.$$

$$-14{\cdot}04 - 1 = \log c_1$$

$$-15{\cdot}04 = \log c_1$$

$$\overline{16}{\cdot}96 = \log c_1$$

$$9{\cdot}12 \times 10^{-16} = c_1$$

The solubility product of AgI

$$= 9{\cdot}12 \times 10^{-16} \times 1 \times 10^{-1}$$

$$= 9{\cdot}12 \times 10^{-17}$$

$$= 91{\cdot}2 \times 10^{-18}.$$

The solubility of AgI $= \sqrt{91{\cdot}2 \times 10^{-18}}$

$$= 9{\cdot}55 \times 10^{-9}.$$

Ans. Solubility of AgI at 18° is $9{\cdot}55 \times 10^{-9}$ gram mol / *l*.

Problem 205. The distribution coefficient of ammonia between water and chloroform is 26·3. An aqueous solution containing copper sulphate and ammonia in the ratio 1 : 18 gram molecules was shaken up with chloroform; after equilibrium had been attained, one litre of the chloroform phase contained 0·225 gram of ammonia whereas the same volume of the aqueous solution contained 7·650 grams of ammonia. Calculate the ratio in which copper and ammonia combine to form complex copper ammonium ion.

Solution : $\frac{NH_3 \text{ in water}}{NH_3 \text{ in chloroform}} = 26{\cdot}3.$

$$\frac{NH_3 \text{ in water}}{0{\cdot}225} = 26{\cdot}3.$$

$$NH_3 \text{ in water} = 26{\cdot}3 \times 0{\cdot}225$$

$$= 5{\cdot}919.$$

Thus 5·919 is the amount of free ammonia in water.

∴ 7·650 − 5·919 = 1·731 grams of NH_3 are combined with copper sulphate in water.

To find the amount of copper sulphate present in water: 7·650 + 0·225 = 7·875 grams (or $\frac{7{\cdot}875}{17}$ gram mol) which is the total amount of NH_3 present originally in water.

∴ copper sulphate in water = $\frac{7{\cdot}875}{17 \times 18}$ gram mols that have combined with $\frac{1{\cdot}731}{17}$ gram mols of NH_3.

∴ 1 gram mol of copper sulphate will combine with,

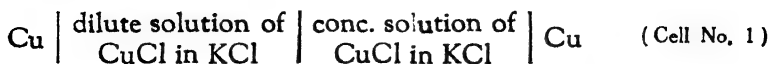
$$\frac{1{\cdot}731}{17} \times \frac{17 \times 18}{7{\cdot}875}$$

i. e., $= 3{\cdot}957.$

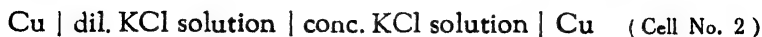
or ≈ 4 gram mols of NH_3.

Ans. Cu : NH_3 : : 1 : 4.

Problem 206. When CuCl is dissolved in KCl solution a complex salt of the formula $(KCl)_n \cdot (CuCl)_m$ is formed, which dissociates giving the ions $K^{\cdot}$ and $Cu_m Cl'_{m+n}$. Two very dilute solutions of CuCl in 0·1N KCl were prepared, the one containing 4 times as much CuCl as the other. The E. M. F. of the cell

Cu | dilute solution of CuCl in KCl | conc. solution of CuCl in KCl | Cu (Cell No. 1)

was 0·0351 volt at 18°. On the assumption that practically the whole of the dissolved CuCl is present as complex salt, and that, on account of the very large excess of KCl over CuCl, the Cl′ ion concentration in the two solutions is the same, and that the dissociation of the KCl and of the complex salt is complete, calculate the value of *m*.

Further, two solutions of KCl, one 0·21 N and the other 0·1 N, and each containing 0·0002 gram-molecule of CuCl per litre, were prepared. The E. M. F. of this cell No. 2

Cu | dil. KCl solution | conc. KCl solution | Cu (Cell No. 2)

was 0·0374 volt at 18°. Calculate the values of *m* and *n*, and give the formula of the complex salt.

Solution : The complex salt $(KCl)_n \cdot (CuCl)_m$ or

$K_nCu_m\ Cl_{m+n}$ dissociates completely into $nK^{\cdot}$ and $Cu_m\ Cl'_{m+n}$.

It must be assumed further that the complex anion

$Cu_m\ Cl'_{m+n}$ also dissociates slightly into $mCu^{\cdot} + (m+n)Cl'$.

$$K = \frac{[Cu^{\cdot}]^m\ [Cl']^{m+n}}{Cu_m\ Cl_{m+n}}.$$

In cell No. 1, for dilute solution

$$K = \frac{[Cu^{\cdot}_d]^m\ [Cl'_d]^{m+n}}{[Cu_m\ Cl_{m+n}]_d}$$

where $Cu^{\cdot}_d$ is $Cu^{\cdot}$, Cl'_d is Cl' and $(Cu_m\ Cl_{m+n})_d$ is undissociated complex anion in dilute solution.

For concentrated solution

$$K = \frac{[Cu^{\cdot}_c]^m [Cl'_c]^{m+n}}{[Cu_m Cl_{m+n}]_c} .$$

Since Cl′ ions are derived from KCl which is 0·1N in both dilute and concentrated solutions,

$$[Cl'_d]^{m+n} = [Cl'_c]^{m+n}$$

The concentrated solution contains 4 times as much CuCl as the dilute one.

$$\therefore \quad (Cu_m Cl_{m+n})_c = 4 (Cu_m Cl_{m+n})_d$$

$$\therefore \quad \frac{[Cu^{\cdot}_d]^m [Cl'_d]^{m+n}}{[Cu_m Cl_{m+n}]_d} = K = \frac{[Cu^{\cdot}_c]^m [Cl'_c]^{m+n}}{4 [Cu_m Cl_{m+n}]_d}$$

$$\frac{[Cu^{\cdot}_d]^m}{[Cu^{\cdot}_c]^m} = \frac{[Cu_m Cl_{m+n}]_d}{4 [Cu_m Cl_{m+n}]_d}$$

$$\left[\frac{Cu^{\cdot}_d}{Cu^{\cdot}_c}\right]^m = \frac{1}{4}$$

Substituting this value in the following equation :

$$E = 0{\cdot}058 \log \frac{Cu^{\cdot}_d}{Cu^{\cdot}_c} , \text{ where}$$

E is negative, since Cu electrode in dilute solution is negative,

$$\text{one gets} \quad -0{\cdot}0351 = 0{\cdot}058 \times \log \left(\frac{1}{4}\right)^{\frac{1}{m}}$$

$$= 0{\cdot}058 \times \log (0{\cdot}25)^{\frac{1}{m}}$$

$$= -0{\cdot}058 \times \frac{1}{m} \times 0{\cdot}6021.$$

$$\therefore \quad m = \frac{.0{\cdot}058 \times 0{\cdot}6021}{0{\cdot}0351}$$

$$= 0{\cdot}9949$$

$$\text{or,} \quad \approx 1.$$

In cell No. 2,

$$\frac{[Cu^{\cdot}_d]^m [Cl'_d]^{m+n}}{[Cu_m Cl_{m+n}]_d} = \frac{[Cu^{\cdot}_c]^m [Cl'_c]^{m+n}}{[Cu_m Cl_{m+n}]_c}$$

In this cell the amount of CuCl is the same in both the dilute and the concentrated solution.

$$\therefore \quad [Cu_m\, Cl_{m+n}]_d = [Cu_m\, Cl_{m+n}]_c$$

The strength of KCl in dilute solution is 0·1 N while in the concentrated one it is 0·21 N.

$$\therefore \quad [Cl'_d]^{m+n} = [0{\cdot}1]^{m+n}$$

$$\text{and} \quad [Cl'_c]^{m+n} = [0{\cdot}21]^{m+n}$$

Substituting these values in the above equation :

$$\frac{[Cu^{\cdot}_d]^m\,[0{\cdot}1]^{m+n}}{[Cu_m\, Cl_{m+n}]_d} = \frac{[Cu^{\cdot}_c]^m\,[0{\cdot}21]^{m+n}}{[Cu_m\, Cl_{m+n}]_d}$$

$$\frac{[Cu^{\cdot}_d]^m}{[Cu^{\cdot}_c]^m} = \frac{[0{\cdot}21]^{m+n}}{[0{\cdot}1]^{m+n}}$$

$$\left[\frac{Cu^{\cdot}_d}{Cu^{\cdot}_c}\right]^m = [2{\cdot}1]^{m+n}$$

$$\frac{Cu^{\cdot}_d}{Cu^{\cdot}_c} = (2{\cdot}1)^{\frac{m+n}{m}}.$$

Substituting this value in the following equation :

$$E = 0{\cdot}058 \log \frac{Cu^{\cdot}_d}{Cu^{\cdot}_c},$$

$$\text{one gets } 0{\cdot}0374 = 0{\cdot}058 \log (2{\cdot}1)^{\frac{m+n}{m}}.$$

$$0{\cdot}0374 = 0{\cdot}058 \times \frac{m+n}{m} \times 0{\cdot}3222$$

$$\frac{m+n}{m} = \frac{0{\cdot}0374}{0{\cdot}058 \times 0{\cdot}3222}$$

$$= 2{\cdot}002.$$

Since, $m = 1$, $n = 1{\cdot}002$, or ≈ 1.

The complex salt is, therefore, KCl CuCl or $KCuCl_2$.

Ans. (1) $m = 1$, and $n = 1$.

(2) The complex salt is $KCuCl_2$.

Problem 207. The percentage of hydrolysis in 0·1 N KCN solution is 0·88. If the dissociation constant for HCN is $1{\cdot}3 \times 10^{-9}$, calculate the ionisation constant of water.

Solution: $KCN + H_2O = K^{\cdot} + OH' + HCN.$

It is assumed that KOH and KCN are completely dissociated.

The concentration of OH′ and HCN will be,

$$\frac{0{\cdot}1 \times 0{\cdot}88}{100} = 8{\cdot}8 \times 10^{-4} \text{ N.}$$

and that of CN′ = 0·1 N.

Then, $\dfrac{[H^{\cdot}][CN']}{[HCN]}$ = K, the dissociation constant for HCN.

$$\frac{[H^{\cdot}] \times 0{\cdot}1}{8{\cdot}8 \times 10^{-4}} = 1{\cdot}3 \times 10^{-9}$$

$$[H^{\cdot}] = 1{\cdot}3 \times 10^{-9} \times 8{\cdot}8 \times 10^{-4} \times 10$$

$$= 114{\cdot}4 \times 10^{-13}$$

$$[H^{\cdot}][OH'] = 114{\cdot}4 \times 10^{-13} \times 8{\cdot}8 \times 10^{-4}$$

$$= 1006 \times 10^{-17}.$$

$$= 1{\cdot}006 \times 10^{-14}.$$

Ans. The ionisation constant of water is $1{\cdot}006 \times 10^{-14}$.

Problem 208. The following figures were obtained for the inversion of cane sugar in the presence of 0·5 N $Al(NO_3)_3$ solution at 80°C.

t (min.)	0	45·7	76·8	∞
a°	10·50	3·15	0·33	− 3·08

where *a*° is the polarisation of the solution. The inversion constant in the presence of 0·001N HNO_3 (completely dissociated) using time in minutes is 0·00225. Calculate the degree of hydrolysis of $Al(NO_3)_3$ solution at 80°C.

Solution: Find the inversion constant in the presence of 0·5 N $Al(NO_3)_3$ using the equation for monomolecular reaction;

$$K = \frac{2 \cdot 302}{t} \log \frac{a}{a - x}$$

(1)
$$t = 45 \cdot 7 \text{ min.};$$
$$a = (10 \cdot 50 + 3 \cdot 08 =)\ 13 \cdot 58$$
$$a - x = (3 \cdot 15 + 3 \cdot 08 =)\ 6 \cdot 23.$$

Substituting the values in the above equation,

$$K = \frac{2 \cdot 302}{45 \cdot 7} \log \frac{13 \cdot 58}{6 \cdot 23}$$
$$= \frac{2 \cdot 302 \times 0 \cdot 3377}{45 \cdot 7}$$
$$= 0 \cdot 01700.$$

(2)
$$t = 76 \cdot 8;$$
$$a = 13 \cdot 58;$$
$$a - x = 3 \cdot 41.$$
$$\therefore \quad K = \frac{2 \cdot 302}{76 \cdot 8} \log \frac{13 \cdot 58}{3 \cdot 41}$$
$$= \frac{2 \cdot 302 \times 0 \cdot 6}{76 \cdot 8}$$
$$= 0 \cdot 01797.$$

The mean of (1) and (2) = 0·01748.

On the assumption that the inversion constant is proportional to the concentration of the acid, the concentration of the HNO_3 formed by the hydrolysis of $Al(NO_3)_3$ will be,

$$[HNO_3] = \frac{0 \cdot 001 \times 0 \cdot 01748}{0 \cdot 00225}$$
$$= 0 \cdot 007767.$$

Now if x be the degree of hydrolysis of $Al(NO_3)_3$ the concentration of HNO_3 so formed will be $0 \cdot 5 \times x$

$$\text{or,} \quad 0{\cdot}5\,x = 0{\cdot}007767$$

$$x = \frac{0{\cdot}007767}{0{\cdot}5}$$

$$= 0\ 01553$$

Ans. The degree of hydrolysis of 0·5 N $Al(NO_3)_3$ at 80°C. is 0·01553 or 1·553 per cent.

Problem 209. The hydrolysis of $\frac{N}{32}$ methyl acetate at 100°C. by $\frac{N}{500}$ HCl proceeds as follows:— *a* is the titre of 10 c.c. of the solution at time *t* minutes.

t	0	64	113	152	∞	
a	1·10	4·15	6·03	7·35	15·70	c.c. N/50 NaOH.

If the velocity constant for the hydrolysis of $\frac{N}{32}$ methyl acetate by a solution of $AlCl_3$ containing $\frac{1}{32}$ gram molecule per litre is 0·00216 at 100°C., calculate the degree of hydrolysis of $AlCl_3$ solution, assuming the velocity constant to be proportional to the concentration of HCl.

Solution : Find the velocity constant K for $\frac{N}{500}$ HCl with the help of the formula for a monomolecular reaction.

$$K = \frac{2{\cdot}302}{t} \log \frac{a}{a - x}$$

$$a = (15{\cdot}70 - 1{\cdot}10) = 14{\cdot}60$$

$$(1)\ t = 64; \quad a = 14{\cdot}6;\ a - x = (15{\cdot}70 - 4{\cdot}15 =)\ 11{\cdot}55$$

$$K = \frac{2{\cdot}302}{64} \log \frac{14{\cdot}60}{11{\cdot}55} = 0{\cdot}003659.$$

(2) $t = 113$; $a = 14{\cdot}60$; $a - x = (15{\cdot}70 - 6{\cdot}03 =) \; 9{\cdot}67$

$$K = \frac{2{\cdot}302}{113} \log \frac{14{\cdot}60}{9{\cdot}67} = 0{\cdot}003646.$$

(3) $t = 152$; $a = 14{\cdot}60$; $a - x = (15{\cdot}70 - 7{\cdot}35) = 8{\cdot}35$

$$K = \frac{2{\cdot}302}{152} \log \frac{14{\cdot}60}{8{\cdot}35} = 0{\cdot}003674.$$

The mean of the above three constants $= 0{\cdot}0036596$.

The velocity constant for $\frac{1}{32}$ gram molecule of $AlCl_3$ is equal to 0·00216. Assuming that the velocity constant to be proportional to the concentration of HCl, the concentration of HCl produced by the hydrolysis of $AlCl_3$

$$= \frac{0{\cdot}00216}{0{\cdot}0036596} \times \frac{N}{500}$$

$$= 0{\cdot}00118 \text{ N}.$$

The hydrolysis of $AlCl_3$ proceeds as,

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl.$$

If x be the degree of hydrolysis of $\frac{1}{32}$ gram mol of $AlCl_3$, the concentration of HCl so produced will be $\frac{3xN}{32}$

$$\therefore \frac{3xN}{32} = 0{\cdot}00118 \text{ N}$$

$$x = \frac{0{\cdot}00118 \times 32}{3}$$

$$= 0{\cdot}01259$$

Ans. The degree of hydrolysis of $AlCl_3$ ($\frac{1}{32}$ gram mol) is 0·01259 or 1·259 per cent.

Problem 210. At 25°C. the dissociation constant of aniline is $4{\cdot}8 \times 10^{-10}$, and that of acetic acid $1{\cdot}8 \times 10^{-5}$. The ionic product of water is $1{\cdot}2 \times 10^{-14}$. Calculate the pH of 0·5 N

solution of aniline acetate, if the unhydrolysed aniline acetate is assumed to be completely dissociated.

***Solution*:** Let x be the degree of hydrolysis of aniline acetate.

0·05 x aniline and 0·05 x acetic acid.

0·05 $(1 - x)$ aniline acetate unhydrolysed which gives

0·05 $(1 - x)$ aniline˙ and

0·05 $(1 - x)$ acetate′.

The dissociation constant of acetic acid K_{ac} :

$$K_{ac} = \frac{[H^{\cdot}][0{\cdot}05(1-x)]}{0{\cdot}05x} = 1{\cdot}8 \times 10^{-5}$$

$$\text{or, } [H^{\cdot}] = \frac{1{\cdot}8 \times 10^{-5} \times 0{\cdot}05x}{0{\cdot}05(1-x)} = \frac{1{\cdot}8 \times 10^{-5} \times x}{1-x}.$$

[OH′] from ionic product of water :

$$[OH'] = \frac{1{\cdot}2 \times 10^{-14} \times (1-x)}{1{\cdot}8 \times 10^{-5} \times x}.$$

The dissociation constant of aniline:

$$\frac{[OH'][\text{aniline}^{\cdot}]}{[\text{aniline}]} = 4{\cdot}8 \times 10^{-10}$$

$$4{\cdot}8 \times 10^{-10} = \frac{1{\cdot}2 \times 10^{-14} \times (1-x) \times 0{\cdot}05(1-x)}{1{\cdot}8 \times 10^{-5}x \times 0{\cdot}05x}$$

$$= \frac{(1-x)^2}{x^2} \times \frac{1{\cdot}2 \times 10^{-14}}{1{\cdot}8 \times 10^{-5}}$$

$$\left(\frac{1-x}{x}\right)^2 = \frac{4{\cdot}8 \times 10^{-10} \times 1{\cdot}8 \times 10^{-5}}{1{\cdot}2 \times 10^{-14}}$$

$$= 0{\cdot}72.$$

$$\therefore \quad \frac{1-x}{x} = 0{\cdot}8484; \quad \frac{1}{x} - 1 = 0{\cdot}8484; \quad \frac{1}{x} = 1{\cdot}8484.$$

$$\therefore \quad x = \frac{1}{1{\cdot}8484} = 0{\cdot}5420 \text{ or } 54{\cdot}2\,\% \text{ hydrolysis.}$$

$$[H^{\cdot}] = \frac{1 \cdot 8 \times 10^{-5} \times x}{1 - x}$$

$$= \frac{1 \cdot 8 \times 10^{-5} \times 0 \cdot 5420}{(1 - 0 \cdot 5420)}$$

$$= 2 \cdot 13 \times 10^{-5}$$

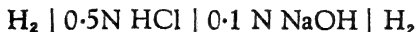
$$\log [H^{\cdot}] = \bar{5} \cdot 3284$$

$$= - 4 \cdot 6716.$$

$$pH = 4 \cdot 67.$$

Ans. The pH is 4·67.

Problem 211. The E. M. F. of the cell

$$H_2 \mid 0 \cdot 5N\ HCl \mid 0 \cdot 1\ N\ NaOH \mid H_2$$

at 25°C. is 0·721 volts. If the H_2 at each electrode is under atmospheric pressure and if the diffusion potential is neglected, calculate the pH and the degree of ionisation of the NaOH solution, given that the pH of the HCl solution is 0·3615 and the ionic product of water $1 \cdot 2 \times 10^{-14}$.

Solution : First find [H˙] in 0·5 N HCl solution.

$$pH = 0 \cdot 3615$$

$$\therefore \quad \log [H^{\cdot}] = - 0 \cdot 3615$$

$$= \bar{1} \cdot 6385$$

$$\therefore \quad [H^{\cdot}] = 0 \cdot 435 \text{ gram equivalent} / l.$$

Substituting this value and that of E. M. F. in the equation :

$$E = \frac{0 \cdot 058}{n} \log \frac{c_1}{c_2},$$

one gets,

$$0 \cdot 721 = \frac{0 \cdot 058}{n} \log \frac{0 \cdot 435}{c_2}$$

$$\therefore \quad \frac{0 \cdot 721}{0 \cdot 058} = - 0 \cdot 3615 - \log c_2$$

$$12 \cdot 43 + 0 \cdot 3615 = - \log c_2$$

$$\therefore \quad pH = 12 \cdot 7915.$$

To calculate the degree of ionisation of 0·1N NaOH, first find the [$H^{\cdot}$] in that solution.

$$-\log c_2 = 12{\cdot}7915$$

$$\log c_2 = -12{\cdot}7915$$

$$= \overline{13}{\cdot}2085$$

$$\therefore \quad c_2 = 1{\cdot}616 \times 10^{-13} \text{ gram equivalent / litre.}$$

The ionic product of water is 1·2 × 10^{-14}

$$\text{or } [H^{\cdot}][OH'] = 1{\cdot}2 \times 10^{-14}$$

$$1{\cdot}616 \times 10^{-13} \times [OH'] = 1{\cdot}2 \times 10^{-14}$$

$$[OH'] = \frac{1{\cdot}2 \times 10^{-14}}{1{\cdot}616 \times 10^{-13}}$$

$$= 0{\cdot}07424$$

The degree of ionisation of 0·1 N NaOH

$$= \frac{0{\cdot}07424}{0{\cdot}1}$$

Ans. (1) The pH is 12·7915 ;
(2) The degree of ionisation is 0·7424.

Problem 212. The dissociation constant of HCN is 1·3 × 10^{-9} and the ionic product of water is 1·0 × 10^{-14}. What is the percentage of hydrolysis of $\frac{N}{100}$ solution of NaCN ?

Solution : If x be the degree of hydrolysis of 0·01N NaCN, then NaOH = 0·01x, and HCN = 0·01x.

$$[OH'] = 0{\cdot}01x, \text{ as NaOH is completely ionised.}$$

$$[H^{\cdot}] = \frac{1{\cdot}0 \times 10^{-14}}{0{\cdot}01x}$$

$$[CN'] = 0{\cdot}01(1 - x), \text{ as NaCN is completely ionised.}$$

$$\frac{[H^{\cdot}][CN']}{[HCN]} = \frac{1{\cdot}0 \times 10^{-14} \times 0{\cdot}01(1 - x)}{0{\cdot}01x} \times \frac{1}{0{\cdot}01x}$$

$$\therefore \quad 1{\cdot}3 \times 10^{-9} = \frac{1{\cdot}0 \times 10^{-14} \times (1 - x)}{0{\cdot}01 \times x^2}$$

$$\therefore \quad x^2 = \frac{1{\cdot}0 \times 10^{-14} \times (1 - x)}{0{\cdot}01 \times 1{\cdot}3 \times 10^{-9}}$$

As x is very small compared to 1, $1 - x$ becomes 1, then

$$x^2 = \frac{1{\cdot}0 \times 10^{-14}}{1{\cdot}3 \times 10^{-11}}$$

$$\therefore \quad x = \sqrt{\frac{1{\cdot}0 \times 10^{-3}}{1{\cdot}3}}$$

$$= 0{\cdot}02773 \quad \text{or} \quad 2{\cdot}773 \text{ per cent.}$$

Ans. The percentage of hydrolysis of $\frac{N}{100}$ NaCN is 2·773.

Problem 213. Find the solubility product of magnesium hydroxide from the following data :—

The precipitation of mangnesium hydroxide on adding an alkali solution drop by drop to 0·00025 molar solution of magnesium chloride is followed by a hydrogen electrode against a calomel electrode, and the value of E. M. F. when precipitation begins is 0·892. $pK_w = 14{\cdot}1$ and E. M. F. of calomel elεctrode = 0·283.

Solution : $0{\cdot}283 - E\,(\text{observed}) = 0{\cdot}058 \log H^{\cdot}$

$$0{\cdot}283 - 0{\cdot}892 = 0{\cdot}058 \log H^{\cdot}$$

$$-\ 0{\cdot}609 = 0{\cdot}058 \log H^{\cdot}$$

$$-\frac{0{\cdot}609}{0{\cdot}058} = \log H^{\cdot}$$

$$-\ 10{\cdot}6 = \log H^{\cdot}$$

$$10^{-10.6} = H^{\cdot}$$

The ionic product, $K_w = H^{\cdot} \times OH' = 10^{-14.1}$

$$\therefore \quad 10^{-10.6} \times OH' = 10^{-14.1}$$

$$OH' = 10^{-3.5}$$

Solubility product of $Mg(OH)_2$ $= Mg^{\cdot\cdot} \times (OH')^2$

$$= 2{\cdot}5 \times 10^{-4} \times (10^{-3{\cdot}5})^2$$
$$= 2{\cdot}5 \times 10^{-4} \times 10^{-7}$$
$$= 2{\cdot}5 \times 10^{-11}.$$

Ans. The solubility product is $2{\cdot}5 \times 10^{-11}$.

Problem 214. The E. M F. of the cell

$$Ag \mid AgCl \mid ZnCl_2,\ 5\,H_2O \mid Zn$$

is given by $E = 1{\cdot}015 - 2{\cdot}1 \times 10^{-4}(T - 283)$. Calculate the heat of reaction :

$$Zn + 2\,AgCl = ZnCl_2 + 2\,Ag$$

at 0°C. (1 Volt-coulomb = 0·238 cal.; F = 96540 coulombs).

Solution : Use the affinity equation :

$$A = nFE \text{ volt-coulombs}$$
$$= 0{\cdot}238nFE \text{ calories.}$$

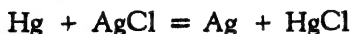
$$E \text{ at } 0°C. = 1{\cdot}015 - 2{\cdot}1 \times 10^{-4}(273 - 283)$$
$$= 1{\cdot}015 + 2{\cdot}1 \times 10^{-4} \times 10$$
$$= 1{\cdot}015 + 0{\cdot}0021.$$
$$= 1{\cdot}0171.$$

Substituting the value of E in the above equation,

$$A = 0{\cdot}238 \times 2 \times 96540 \times 1{\cdot}0171$$
$$= 46737 \text{ calories}$$

Ans. The heat of reaction is 46737 calories.

Problem 215. The heat of reaction

$$Hg + AgCl = Ag + HgCl$$

is – 3369 cals. If the temperature coefficient of the E. M. F. of the cell :

$$Hg \mid HgCl \text{ KCl sol.} \mid AgCl \text{ KCl sol.} \mid Ag$$

is 0·000338 volt per degree, calculate the affinity of the reaction at 25°C. Show by means of an arrow the direction in which the current flows inside the cell.

Solution : First find the E. M. F. of the cell at 25°C.

$$E = \frac{Q}{nF} + T\frac{dE}{dT}$$

$$= \frac{Q}{23040n} + T\frac{dE}{dT} \text{ where F is expressed in cals.}$$

Substituting the respective values in the above,

$$\frac{-3369}{23040} + 298 \times 3{\cdot}38 \times 10^{-4}$$

$$= -0{\cdot}1462 + 0{\cdot}1007$$

$$= -0{\cdot}0455.$$

The affinity $A = nFE$

$$= 23040nE$$

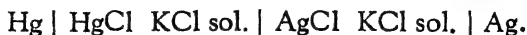
$$= -23040 \times 0{\cdot}0455$$

$$= -1048.$$

Ans. (*a*) The affinity = – 1048.

(*b*) The current inside the cell will flow from Hg to Ag.

Hg | HgCl KCl sol. | AgCl KCl sol. | Ag.

⟶

Problems for Solution

Problem 216. An electric current was passed simultaneously through the following solutions : hydrochloric acid, ferrous sulphate, ferric sulphate, and silver potassium cyanide. If 5·2 litres of hydrogen (at N. T. P.) were evolved from the hydrochloric acid solution, how much metal would be deposited in the case of iron and silver salts ?

Ans. Iron (Ferrous) = 13·0, Iron (Ferric) = 8·67 and Silver = 50·14, grams respectively.

Problem 217. An electric current is passed through a series of cells containing respectively (1) acidified water, (2) aqueous solution of common salt, (3) copper sulphate, (4) silver nitrate and (5) potassium acetate. What is the nature and amount of substances liberated in each cell if the current is allowed to pass until 50 c. c. of oxygen (at N. T. P.) have been liberated in the first ?

Ans.	Cathode	Anode
1st cell	100 c. c. H_2;	50 c. c. O_2;
2nd cell	100 c. c. H_2; 0·3572 g NaOH.	100 c. c. Cl_2; (less amount dissolved)
3rd cell	0·2835 g Cu	50 c. c. O_2; 0·4375 g H_2SO_4
4th cell	0·9654 g Ag	50 c. c. O_2; 0·5623 g HNO_3
5th cell	100 c. c. H_2; 0·500 g KOH	100 c. c. C_2H_6 200 c. c. CO_2

Problem 218. Find the pH at which methyl red can be used as an indicator given that its dissociation constant is $7{\cdot}9 \times 10^{-6}$.

Ans. From 4·1 to 6·1 pH.

Problem 219. Calculate the degree of ionisation in each of the following solutions of acetic acid ; find also the dissociation constant of the acid. (Temp. = 25°)

V (liters)	128	256	∞
Mol. conductivity	16·99	23·82	364

Ans. (*a*) Degree of ionisation of acetic acid : 0·0467 ; 0·0654

(*b*) Dissociation constant (v in c. c.) : $1{\cdot}785 \times 10^{-8}$; $1{\cdot}791 \times 10^{-8}$

Problem 220. A gram moleculer weight of an acid is contained in 30·15, 60·3, and 120·6 litres of solutions respectively. The observed resistances for these concentrations are (i) 92·9 ohms, (ii) 135·4 ohms, and (iii) 200 ohms. The resistance of $\frac{N}{50}$ potassium chloride is 57 ohms in the same cell, and the molecular conductivity for potassium chloride of the same strength is 129·7. Calculate the value of K for each concentration. ($\mu\infty$ for the acid is 350.)

Ans. $71{\cdot}91 \times 10^{-8}$; $71{\cdot}93 \times 10^{-8}$; $71{\cdot}78 \times 10^{-8}$ (v in c.c.).

Problem 221. Calculate from the following data the volume of the solution which contains 1 gram molecule of silver chloride at 13·8°. The ratio of known resistance to that of the cell and contents is 1 : 53·02, the known resistance being 2140 ohms; limiting ionic conductivities of Ag and Cl are respectively 45·8 and 55·4. Cell constant K = 111·7.

Ans. 102800 litres.

Problem 222. Given that the specific conduction of water at 18° is $0{\cdot}038 \times 10^{-6}$ mhos and that the ionic condutivities at infinite dilution of hydrion and hydroxidion are 318 and 174 respectively. Calculate the degree of ionisation of water, in gram mols per litre.

Ans. $7{\cdot}7 \times 10^{-8}$ gram mol / litre.

Problem 223. Phenolphthalein readily shows the presence of $H^{\cdot}$ or $(OH)'$ ions when their concentration in a solution exceeds 10^{-5} normal. Calculate the $(OH)'$ ion concentration in $\frac{N}{10}$ solution of C_6H_5ONa and show that it should react alkaline towards phenolphthalein. The dissociation constant of water is $1{\cdot}2 \times 10^{-14}$ and that of phenol is $1{\cdot}3 \times 10^{-10}$.

Ans. $OH' = 3{\cdot}39 \times 10^{-3}$.

Problem 224. Aluminium is manufactured by electrolysing a mixture of alumina, aluminium fluoride, and sodium fluoride. The heat of combustion of Al_2O_3 is 392 cals.; of AlF_3 is 249 cals.; of NaF is 102·6 cals., all being stated in large calories

per gram molecule. The current is passed from one electrode to the other at a pressure of 6 volts. State what reactions occur and why? And calculate the fraction of the energy which is used in producing aluminium, and also state what use is made of the balance. (One large calorie = 4200 joules. One gram equivalent requires 96540 coulombs).

Ans. (i) The main reaction is the decomposition of Al_2O_3 as it requires the least amount of energy. (ii) The fraction of energy used = 47·4 %. (iii) The balance of the energy is used for heating the mixture to the required temperature.

***Problem* 225.** The velocity of migration of the silver ion at 18°C. is 0·000577 cm. per second and that of the nitrate ion is 0·000630 cm. per second. Calculate the equivalent conductivity of 0·1N silver nitrate solution, if the van't Hoff factor (i) is 1·8. All observations are made at the same temperature. (F = 96540 coulombs).

Ans. 93·168 equivalent conductivity.

***Problem* 226.** It is required to mix 0·1N, CH_3COOH (K acetic acid = $1{\cdot}8 \times 10^{-5}$) with $CH_2OHCOOH$ (K glycollic acid = 15×10^{-5}) in such a way that there is no change in the hydrogen ion concentration. What concentration of glycollic acid is required?

Ans. 0·012 N.

***Problem* 227.** A 5 per cent. solution of cane sugar has a rotation of a° = + 66·7° in a 2 cm. tube. After complete inversion of the solution it is − 19·7°. If the solution is 0·01N with respect to hydrogen chloride, the angle of rotation decreases by 68·2° in 20 minutes. What is the velocity constant of inversion? What would be the value of the velocity constant if the hydrogen chloride were replaced by 0·1 N lactic acid, the dissociation constant of which is $1{\cdot}4 \times 10^{-4}$. The hydrogen chloride may be taken as completely dissociated in 0·01N solution. (*N. B.*—v is in litres in dissociation constant)

Ans. 0·07785; 0·02859.

Problem 228. A current which deposited 0·161 gram of silver in a silver voltameter was passed through a solution of silver nitrate. After the experiment, the anode liquid gave 1·6347 gram of AgCl, and equal volume of the solution before the experiment gave 1·7463 gram of AgCl. Calculate the transport number of the ions of the solution.

Ans. Transport number of

$Ag^{\cdot}$ ions = 0·478; NO_3' ions = 0·522.

Problem 229. From the electrolysis of hydrochloric acid in a cell with cadmium anode the following results were obtained: change in concentration of chlorine at anode and cathode was respectively ± 0·00545 gram and silver deposited in voltameter connected in series with the cell weighed 0·0986 gram. Calculate the transport numbers of hydrogen and chlorine.

Ans. Transport number of

$H^{\cdot}$ ions = 0·832 and that of Cl' ions = 0·168.

Problem 230. A current which deposited 0·047 gram of copper in a voltameter containing copper sulphate was passed through a solution of silver nitrate using silver electrodes. The liquid from the cathode contained, before the experiment, 1·315 gram of silver, and after the experiment, 1·231 gram of Ag. Calculate the transport number of the ions in solution.

Ans. Transport number of

$Ag^{\cdot}$ ions = 0·475 and that of NO_3 ions = 0·525.

Problem 231. A solution of potassium chlorate is electrolysed, and during electrolysis 0·3514 gram of silver is deposited in a silver voltameter in series. 41·079 grams of solution gave before electrolysis 1·0576 gram of potassium sulphate. The anode solution after electrolysis weighed 59·954 grams and gave 1·3802 grams of potassium sulphate. The anode was cadmium and was not attacked by chlorate ions. Find the transport number of the cation.

Ans. Transport number of cation = 0·5759.

***Problem* 232.** Calculate the transport number of the cation from the following experimental data :— A current of 0·9 milli-ampere was passed through $\frac{N}{100}$ solution of silver nitrate between silver electrodes for 6 hours and 52 minutes. After the experiment, 14·22 c. c. (the total anode solution) required 6·90 c. c. of $\frac{N}{25 \cdot 56}$ HCl for complete precipitation.

Ans. Transport number of the cation = 0·4458.

***Problem* 233.** A solution containing 0·1605 per cent. NaOH was electrolysed between platinum electrodes. After electrolysis, 55·25 grams of the cathode solution contained 0·09473 gram NaOH, whilst the concentration of the middle portion of the electrolyte was unchanged. In a silver voltameter in series, silver equivalent to 0·029 gram NaOH was deposited during electrolysis. Calculate the transport numbers of the $Na^{\cdot}$ and OH' ions.

Ans. Transport numbers of
$Na^{\cdot}$ = 0·209 and OH' = 0·791.

***Problem* 234.** Three litres of a solution of 2N HCl is divided by diaphragms into three equal parts :— Anode (A), Central, and Cathode (K) A current of 5 amperes is passed for 10 hours between unattackable electrodes. Assuming that the transport numbers of $H^{\cdot}$ and Cl' are $\frac{5}{6}$ and $\frac{1}{6}$, calculate the changes in the concentration in A and K, and compare them with the change in concentration which would prevail in the cell if the contents were not separated by diaphragms and were well stirred during electrolysis.

Ans. (1) 11·4 grams will be the fall in concentration of HCl in the cathode chamber.

(2) 56·7 g will be the fall in the anode chamber.

(3) If effectively stirred, the concentration in the anode chamber will fall by 17·01 g and 24·4

g of HOCl will be formed on the assumption that the hydrolysis of the liberated chlorine occurs to the extent of 50 %, the rest of the chlorine remains dissolved in water and that the cell is kept cool.

Problem 235. The specific conductivity of an acetic acid solution, when a mol is dissolved in 18·1 litres of water, is 0·0003464 r-ohms, and that of 0·1N sodium acetate solution is 0·00781 r-ohms. Ionic conductivities of $Na^{\cdot}$ and $H^{\cdot}$ ions at infinite dilution are 44·4 and 311 r-ohms respectively. Assuming that sodium acetate is completely dissociated, calculate the dissociation constant of acetic acid.

Ans. $1{\cdot}789 \times 10^{-5}$.

Problem 236. A solution of $CdCl_2$ containing 0·2016 per cent. of chlorine was electrolysed between Cd anode and a Pt cathode. After electrolysis, 33·59 grams of the anode liquid contained 0·08020 g of chlorine. In a silver voltameter in series with the electrolytic cell, 0·06662 g of silver was deposited during the electrolysis. Calculate the transport number of $Cd^{\cdot\cdot}$ and Cl' ions: (Cl = 35·5 and Ag = 108).

Ans. Transport numbers of

(*a*) $Cd^{\cdot\cdot}$ = 0·43 and (*b*) Cl' = 0·57.

Problem 237. A transport number apparatus contained a solution of $AgNO_3$. Initially 30·6 grams of the solution were equivalent to 8·1 c. c. of $\frac{N}{25}$ KCNS. A silver voltameter placed in series after electrolysis was found to contain $AgNO_3$ equivalent to 7·4 c. c. of KCNS. The anode liquid of the apparatus weighed 20·1 grams and was equivalent to 9·2 c. c. KCNS. Find the transport number of $Ag^{\cdot}$ and NO_3'.

Ans. Transport numbers of

$Ag^{\cdot}$ = 0·4757 and NO_3' = 0·5243.

Problem 238. In a transport number experiment with platinum electrodes, a solution of KOH originally contained 0·200 g of KOH per 100 g of water. After electrolysis, it was found that in the cathode compartment there were 0·180 g of KOH in 60·18 g of the solution. The copper deposited in a voltameter placed in series weighed 0·128 g. Calculate the transport numbers of $K^{\cdot}$ and OH' ions. (Atomic wt. of K is 39 and that of Cu is 63·6).

Ans. Transport numbers of
$K^{\cdot}$ = 0·2643 and OH' = 0·7357.

Problem 239. In a transport number apparatus, a solution of $AgNO_3$ containing 0·0074 g of silver nitrate per gram of water was electrolysed with silver anode. During the experiment 0·0785 g of silver was deposited in a silver voltameter placed in series with the transport number apparatus. After the experiment 25 g of the anode solution contained 0·2553 g of $AgNO_3$. Calculate the transport numbers of the silver and the nitrate ions. (Ag = 107·9, N = 14·0, O = 16.)

Ans. Transport numbers of
$Ag^{\cdot}$ = 0·4313 and NO_3' = 0·5687.

Problem 240. The molecular conductivity of a solution of $AgNO_3$ at infinite dilution is 117. A current of 0·1 ampere is passed for 61 minutes into a decinormal solution of $AgNO_3$. After electrolysis, 50 c. c. of the solution from the cathode chamber required 61·1 c. c. of $\frac{N}{20}$ KCNS solution. Use the data to ascertain (a) the transport number, (b) the ionic velocities, and (c) the absolute velocities of $Ag^{\cdot}$ and NO_3' ions.

Ans. (a) The transport numbers : $Ag^{\cdot}$ = 0·4881 ;
NO_3' = 0·5119 ;

(b) Ionic velocities : $Ag^{\cdot}$ = 57·11 ; NO_3' = 59·89.

(c) Absolute velocities :
(cm. / sec. for a potential gradient of 1 volt / cm.)
$Ag^{\cdot} = 5{\cdot}916 \times 10^{-4}$, $NO_3' = 6{\cdot}203 \times 10^{-4}$.

Problem 241. A solution of NaCl containing 0·2081 gram of NaCl in 100 grams of solution was electrolysed by a current, which deposited 0·4125 g of silver in a coulomb-meter in series with it. The anode solution was now found to contain 0·1375 g of Cl_2 per 100 g of solution. The total weight of anode solution was 718·5 g. Calculate the transport number of Cl′.

Ans. The transport number of Cl′ = 0·5950; it is assumed that the Cl_2 evolved dissolves the anode.

Problem 242. Calculate the solubility product of TlCl and its degree of dissociation in a saturated solution from the following data: the specific conductivity of a saturated solution is 1680×10^{-6} $ohms^{-1}$ at 20°, and the solubility at the same temperature is $1{\cdot}36 \times 10^{-2}$ g mol / *l*. $\Lambda_\infty = 137{\cdot}3$ $ohms^{-1}$.

Ans. (1) Solubility product, $1{\cdot}5 \times 10^{-4}$;
(2) Degree of dissociation, 0·9.

Problem 243. The solubility of uric acid in water at 18°C. is 0·0001506 mols per litre. The molecular conductivity of the saturated solution is 32·24 and the ionic conductivity of anion is 21 and of cation is 318. Find the degree of dissociation of the acid in the pure saturated solution and solubility of the acid in normal hydrochloric acid; the dissociation of hydrochloric acid at this concentration may be taken to be 78 per cent.

Ans. (1) The degree of dissociation = 0·091.
(2) Solubility of uric acid in normal hydrochloric acid = $2{\cdot}818 \times 10^{-10}$ gram mols per litre.

Problem 244. The E. M. F. of the cell

$$Ag \;\Big|\; \begin{matrix}Ag\,Cl \text{ in} \\ 0{\cdot}1N\ KCl\end{matrix} \;\Big|\; \begin{matrix}\text{saturated} \\ NH_4NO_3\end{matrix} \;\Big|\; 0{\cdot}1N\ Ag\,NO_3 \;\Big|\; Ag$$

is $-0{\cdot}450$ volt at 25°C. 0·1N KCl is 85 per cent. dissociated and 0·1N $AgNO_3$, 82 per cent. Calculate the solubility product of AgCl, assuming that diffusion potential is eliminated and $\frac{2{\cdot}3\,RT}{F} = 0{\cdot}059$.

Ans. $1{\cdot}649 \times 10^{-10}$.

Problem 245. A cell is arranged by having one electrode, a platinum plate surrounded by an atmosphere of hydrogen over a normal solution of an alkali (80 per cent. dissociated), and the other electrode, an atmosphere of hydrogen over a normal solution of acid (80 per cent. dissociated). Calculate the E. M. F. given by this cell, neglecting the P. D. at the boundary of the solutions, and state what change accompanies the discharge.

Ans. (1) The E. M. F. given by the cell is 0·7573.
(2) Hydrogen will be liberated at the cathode and oxygen at the anode.

Problem 246. Calculate the E. M. F. of the Daniel cell given that $Zn + CuSO_4 = ZnSO_4 + Cu + 50110$ cals. 1 volt-coulomb = 0·24 cal.; 1 Faraday = 96540 coulombs. Temp. coefficient = − 0·000034 volt per degree.

Ans. 1·070 − 0·000034 *t*.

Problem 247. What is the total E. M. F. at 18° of the cell

$$H_2 \mid 0{\cdot}1N\ HCl \mid 0{\cdot}001N\ HCl \mid H_2$$

if the H_2 at each electrode is at atmospheric pressure? The 0·1N HCl is 92 per cent. dissociated and the 0·001N HCl is completely dissociated. The ionic conductivity of $H^{\cdot}$ is 318 and of Cl' is 65·4.

Ans. 0·1889 volt.

Problem 248. The normal potential of copper and silver are 0·34 and 0·80 volt respectively. Calculate the E.M.F. of the cell

$$Cu \mid 0{\cdot}1\ Mol\ CuSO_4 \mid AgCl\ (\text{sat. solution}) \mid Ag$$

at 25°, if the concentration of silver ions in the saturated solution of AgCl is $1{\cdot}25 \times 10^{-5}$ and $CuSO_4$ is 60 per cent. dissociated.

Ans. (1) 0·1977 volt.
Cu is − ve (− 0·3129); Ag is + ve (+ 0·5106).

Problem 249. Find the E. M. F. of the cell

$$\text{Ag} \left| \begin{matrix} 0\cdot1\text{N KI saturated} \\ \text{with AgI} \end{matrix} \right| \begin{matrix} \text{saturated} \\ NH_4NO_3 \end{matrix} \left| \, 0\cdot1\text{N } AgNO_3 \, \right| \text{Ag}$$

at 25°. 0·1N KI is 88 per cent. dissociated and 0·1N $AgNO_3$, 82 per cent. The solubility product of AgI is $1\cdot0 \times 10^{-16}$. The diffusion potential is eliminated. $\left(\frac{2\cdot3\,RT}{F} = 0\cdot059 \text{ at } 25°C. \right)$

Ans. The E. M. F. is 0·8179 volt.

Problem 250. A concentration cell is made up with silver electrodes immersed in decinormal and centinormal silver nitrate solutions. What is the E. M. F. of the cell at 25°C. ignoring the diffusion E. M. F. at the contact of the two solutions and taking the dissociations of decinormal and centinormal silver nitrate solutions to be respectively 82 % and 84 %?

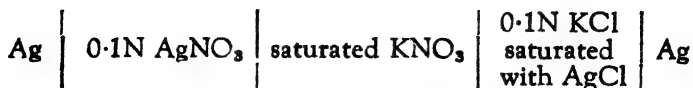
$\left(E = 0\cdot058 \log \frac{c_1}{c_2} \right)$

Ans. The E. M. F. is 0·05738.

Problem 251. Calculate the diffusion potential between 0·025N silver nitrate and 0·0C15N silver nitrate solutions, given that the degree of dissociation of these two solutions are 91·0 per cent. and 98·5 per cent. respectively and that the ionic conductivities of $Ag^{\cdot}$ and NO_3' are 56 and 61 respectively.

Ans. $4\cdot702 \times 10^{-4}$ volts.

Problem 252. The E. M. F. of the cell

$$\text{Ag} \left| \, 0\cdot1\text{N } AgNO_3 \, \right| \text{ saturated } KNO_3 \left| \begin{matrix} 0\cdot1\text{N KCl} \\ \text{saturated} \\ \text{with AgCl} \end{matrix} \right| \text{Ag}$$

is 0·44 volt at 18°. The degrees of dissociation of $AgNO_3$ and KCl solutions are 82 and 85 per cent. respectively. Calculate the solubility of AgCl in g per 100 c. c. of pure water.

Ans. 0·0001925 g.

Problem 253. The normal potential of Zn referred to the $H^{\cdot}$ electrode as zero, is $-0{\cdot}770$ volt and of Cu, 0·329 volt. If excess of Zn is added to a solution of $CuSO_4$, Zn displaces Cu till equilibrium is established. What is the ratio of the concentration of the $Zn^{\cdot\cdot}$ ions to the $Cu^{\cdot\cdot}$ ions at equilibrium ?

Ans. $\dfrac{Zn^{\cdot\cdot}}{Cu^{\cdot\cdot}} = 7{\cdot}94 \times 10^{37}$.

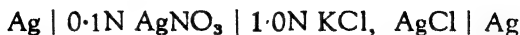
Problem 254. The normal potential of iron referred to the normal hydrogen electrode is $-0{\cdot}46$ volt and of copper, 0·329 volt. When excess of iron is added to a solution of copper sulphate at 25°, iron displaces copper until equilibrium is reached. Calculate the ratio of the concentration of $Fe^{\cdot\cdot}$ to $Cu^{\cdot\cdot}$ ions at equilibrium. $\left(\text{at } 25°,\ E = \dfrac{0{\cdot}058}{n}\log_{10}\dfrac{C}{c}\right)$.

Ans. $1{\cdot}585 \times 10^{27}$.

Problem 255. The normal potential of silver referred to hydrogen electrode as zero is 0·771 volt and that of chlorine at atmospheric pressure is 1·366 volts at 25°C. If the solubility product of silver chloride is 2×10^{-10}, calculate the E. M F of the cell : Ag | a saturated sol. of AgCl | Cl_2 (at atmospheric pressure).

Ans. $-$ 1·167 volts.

Problem 256. The cell :

$$Ag \mid 0{\cdot}1N\ AgNO_3 \mid 1{\cdot}0N\ KCl,\ AgCl \mid Ag$$

has an electromotive force of 0·52 volts neglecting the diffusion potential at 18°C. Assuming complete dissociation of silver nitrate and potassium chloride, find the solubility of AgCl in molecules per litre. $\left(\text{At } 18°\ E = \dfrac{0{\cdot}058}{n}\log_{10}\dfrac{P}{p}\right)$

Ans. $1{\cdot}04 \times 10^{-5}$ mols per litre.

Problem 257. At a given temperature, a litre of saturated silver bromate solution contains 1·9116 grams of the salt; 1 4450 grams of silver nitrate are then added. Calculate the new solubility of the bromate, assuming both the salts to be completely dissociated in solution.

Ans. 0·004895 gram molecule per litre

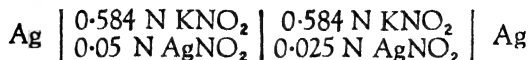
Problem 258. Calculate the E. M. F. of the cell :

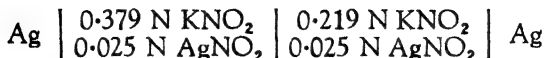
$$Ni \mid 0{\cdot}1 \text{ Mol } NiSO_4 \mid \text{saturated sol. of } AgCl \mid Ag$$

at 25°C. neglecting the liquid junction potential. It is given that nickel sulphate is 60 per cent. dissociated and that the normal potentials of Ni and Ag are $-0{\cdot}22$ and $0{\cdot}80$ volts respectively.

Ans. $-0{\cdot}766$ volt.

Problem 259. When $AgNO_2$ is dissolved in KNO_2 solution, the complex anion $Ag_m(NO_2)_n$ is formed. The E. M. F. at 25°C. of the cell :

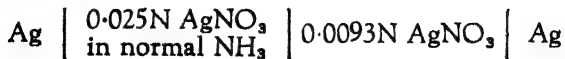
$$Ag \left| \begin{matrix} 0{\cdot}584 \text{ N } KNO_2 \\ 0{\cdot}05 \text{ N } AgNO_2 \end{matrix} \right| \begin{matrix} 0{\cdot}584 \text{ N } KNO_2 \\ 0{\cdot}025 \text{ N } AgNO_2 \end{matrix} \left| Ag \right.$$

is 0·017 volt, and of the cell :

$$Ag \left| \begin{matrix} 0{\cdot}379 \text{ N } KNO_2 \\ 0{\cdot}025 \text{ N } AgNO_2 \end{matrix} \right| \begin{matrix} 0{\cdot}219 \text{ N } KNO_2 \\ 0{\cdot}025 \text{ N } AgNO_2 \end{matrix} \left| Ag \right.$$

is $-0{\cdot}0295$ volt. Assuming that practically the whole of the dissolved $AgNO_2$ exists as a complex ion and that the NO_2' ion concentrations are proportional to the KNO_2 concentrations, calculate the values of m and n, and hence the formula of the complex ion.

Ans. $m = 1{\cdot}04$; $\frac{n}{m} = 2{\cdot}1$; $n = 2$.

The formula of the complex ion is $Ag(NO_2)_2'$.

Problem 260. The E. M. F. of the cell :

$$Ag \left| \begin{matrix} 0{\cdot}025\text{N } AgNO_3 \\ \text{in normal } NH_3 \end{matrix} \right| 0{\cdot}0093\text{N } AgNO_3 \left| Ag \right.$$

at 25°C. is 0·3879 volt. Calculate the dissociation constant of the complex ion $Ag(NH_3)_2$. In the 0·0093 N $AgNO_3$ solution, the silver nitrate may be taken as completely dissociated.

Ans. $1{\cdot}24 \times 10^{-6}$.

Problem 261. Calculate the percentage hydrolysis of sodium acetate in tenth normal solution at 25°, from the following data, assuming that the salt is completely dissociated :— Dissociation constant of acetic acid = 0·000018 ; ionic product for water = $1{\cdot}21 \times 10^{-14}$.

Ans. 0·0082 per cent.

Problem 262. At 25°C. the molecular conductivity of aniline hydrochloride at a dilution of 256 litres is 130·5. At the same dilution, but in the presence of sufficient excess of aniline to practically prevent hydrolysis, it is 107·1. The conductivity of aniline in presence of its hydrochloride may be neglected. The equivalent conductivity of hydrochloric acid at a dilution of 256 litres is 410. Calculate the degree of hydrolysis of aniline hydrochloride at this dilution.

Ans. 7·72 per cent.

Problem 263. The neutralisation of caustic soda by hydrochloric acid (gram equivalents) produces 13700 calories at 18°C. Show that the change of the ionic product of water per 1°C. at 18°C. is about 8 % of the ionic product at that temperature.

Problem 264. The molar conductivity of aniline hydrochloride at 25° is 113·7 r. o. at a dilution of 128 litres per gram molecule. In the presence of excess of aniline, the conductivity is 98 r. o. If the equivalent conductivity for hydrochloric acid at infinite dilution is 383 r. o., calculate the degree of hydrolysis and the hydrolytic constant of the salt, and the dissociation constant of aniline as a base, given $K_w = 1{\cdot}2 \times 10^{-14}$.

Ans. (1) Degree of hydrolysis, 7·528 per cent.

(2) Hydrolytic constant, $4{\cdot}788 \times 10^{-5}$

(3) Dissociation constant of aniline as a base, $2{\cdot}5 \times 10^{-10}$.

Problem 265. In an experiment, one litre of water containing 0·1 gram mol of $C_6H_5NH_2HCl$ was shaken with 50 c. c. of benzene. The benzene layer contains 0·0001 g mol of aniline per c. c. The partition coefficient (benzene / water) = 10. Find the degree of hydrolysis of aniline hydrochloride in water.

Ans. 4·114 per cent.

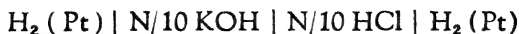
Problem 266. From the following data calculate the hydrogen ion concentration in ammonium acetate solution and show that though a normal solution of the salt is appreciably hydrolysed, it is neutral to all indicators which can detect acidity to the extent of 10^{-5} normal. Dissociation constant of acetic acid is $1{\cdot}8 \times 10^{-5}$ and of ammonium hydroxide is $2{\cdot}3 \times 10^{-5}$. Ionisation constant of water is $1{\cdot}2 \times 10^{-14}$.

Ans. (1) Degree of hydrolysis for N ammonium acetate solution $= 5{\cdot}384 \times 10^{-3}$

(2) $H^{\cdot}$ ion concentration $= 1{\cdot}06 \times 10^{-7}$.

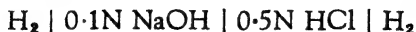
Problem 267. Calculate the ionisation constant of water from the following data :—

The E. M. F. of the cell

$$H_2\,(Pt) \mid N/10\ KOH \mid N/10\ HCl \mid H_2\,(Pt)$$

is equal to 0·6951 volt at 10°C.; N/10 HCl is ionised to the extent of 88·2 per cent. and N/10 KOH, 89·2 per cent.

Ans. $0{\cdot}8106 \times 10^{-14}$.

Problem 268. The E. M. F. of the cell :

$$H_2 \mid 0{\cdot}1N\ NaOH \mid 0{\cdot}5N\ HCl \mid H_2$$

at 25°C. is $-0{\cdot}738$ volt. If hydrogen at each electrode is under atmospheric pressure and if the liq. | liq. potential is neglected, calculate (i) the pH of the NaOH solution and (ii) the ionic product of water, given that the degree of dissociation of 0·1 N NaOH is 0·9 and that of 0·5N HCl is 0·87.

Ans. (i) pH = 12·87; (ii) $K_w = 1{\cdot}2 \times 10^{-14}$.

Problem 269. Calculate the pH of a solution which is 0·1N with respect to acetic acid and sodium acetate. The dissociation constant of acetic acid is $1{\cdot}8 \times 10^{-5}$.

Ans. pH = 4·7447, assuming that sodium acetate is completely dissociated and acetic acid negligibly, and that CH_3COO' ions are supplied by sodium acetate only.

Problem 270. The distribution coefficient of aniline between benzene and water is 10·1. A litre of solution containing 0·03148 gram equivalent of aniline hydrochloride was shaken with 75 c. c. of benzene. After the equilibrium was established, 45 c. c. of the benzene layer were found to contain 0·02624 gram of aniline. Calculate the hydrolytic constant of aniline hydrochloride and the dissociation constant of aniline. ($K_w = 1{\cdot}2 \times 10^{-14}$; molecular weight of aniline = 93).

Ans. Hydrolytic constant, 0·001672
Dissociation constant of aniline, $2{\cdot}055 \times 10^{-10}$

Problem 271. The velocity constant of inversion of cane sugar by 0·25N acetic acid at 25° is $0{\cdot}75 \times 10^{-3}$ Find the value of the constant when the acid solution is also 0·025N with respect to sodium acetate, being given that the dissociation constant of acetic acid is 0·000018, and that the sodium acetate is dissociated to the extent of 86 per cent. (*N. B.*—v is in litres in dissociation constant).

Ans. $0{\cdot}29 \times 10^{-3}$.

Problem 272. Find the E. M. F. of an oxyhydrogen cell from the following data :—

$H_2 + O = H_2O + 67520$ cals. ;
1 Joule = 0·24 cal ;
1 Faraday = 96540 coulombs ;

Temperature coefficient of the cell = − 0·0014 volt per degree.

Ans. $1{\cdot}037 - 0{\cdot}0014\,t$.

Problem 273. Calculate the heat of formation of lead chloride at 498° from the following data :—

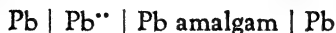
The E. M. F. of the combination :

Cl_2 | molten $PbCl_2$ | Pb

is given by the formula $e = -0{\cdot}000679\,(t - 498)$ volts.
F = 96540 coulombs 1 Joule = 0·2391 cals.

Ans. 82·5 cals.

Problem 274. The temperature coefficient of the cell :

$$Pb \mid Pb^{\cdot\cdot} \mid \text{Pb amalgam} \mid Pb$$

is 0·000016 volts per 1°C. and the E. M. F. at 25° is 0·0057 volt. Calculate (*a*) the latent heat of the cell at 25°C. (*b*) the heat of the reaction at this temperature (*c*) entropy change and (*d*) the change of the free energy.

Ans. (*a*) 0·0477 volt-coulomb (*b*) 1934 cals. (absorbed)
(*c*) 7·37 cals/1° (*d*) − 262·9 cals.

Problem 275. A cell is made up of zinc and silver in contact with the solutions of the respective chlorides. The observed E. M. F. is 1·015 volts at 0°C. The heat of the reaction $2Ag^{\cdot} + Zn = Zn^{\cdot\cdot} + 2Ag$ is 52048 calories. Determine the temperature coefficient of the E. M. F. in the cell. 0·239 calorie = 1 volt-coulomb.

Ans. $-\ 4{\cdot}102 \times 10^{-4}$.

Problem 276. The E. M. F. of the cell :

$$Hg \mid HgCl, \text{ KCl solution} \mid AgCl, \text{ KCl solution} \mid Ag$$

is 0·0455 volt at 25°C. dE/dT = 0·000338 volt / 1°C. Calculate the heat of the reaction : $Hg + AgCl = Ag + HgCl$. 1 volt-coulomb = 0·239 cal.

Ans. − 3369 cals.

Problem 277. The E. M. F. of the combination

$$Hg \mid HgCl\ N\ KCl \mid KNO_3 \mid Hg_2O\ N\ KOH \mid Hg$$

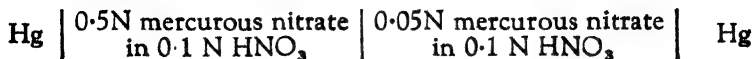
is 0·1483 volt at 18°C., the temperature coefficient is $+\ 8{\cdot}37 + 10^{-4}$ volt per degree. What is the heat of the reaction :

$$HgCl + KOH = \tfrac{1}{2}Hg_2O + \tfrac{1}{2}H_2O + KCl$$

which occurs in the cell ? (1 volt-coulomb = 0·239 cal.)

Ans. − 2193 cals.

Problem 278. Ogg found for the cell :

$$Hg \left| \begin{matrix} 0{\cdot}5N \text{ mercurous nitrate} \\ \text{in } 0{\cdot}1\ N\ HNO_3 \end{matrix} \right| \begin{matrix} 0{\cdot}05N \text{ mercurous nitrate} \\ \text{in } 0{\cdot}1\ N\ HNO_3 \end{matrix} \right| Hg$$

the E. M. F. to be 0·029 volt. Assuming the solution to be completely dissociated, determine the valency of the mercury ion, and hence suggest a formula for mercurous nitrate.

Ans. Valency of mercury (ous) = 1; formula for mercurous nitrate = $Hg_2(NO_3)_2$.

Problem 279. A solution prepared from $MgCl_2$, NH_4OH and $Mg(OH)_2$ was found to contain per litre 2·1 grams $MgCl_2$, 0·61 gram NH_4Cl and 1·4 grams free NH_4OH. The solution was saturated with $Mg(OH)_2$. Taking the dissociation constant of NH_4OH as $1{\cdot}8 \times 10^{-5}$ and assuming $MgCl_2$, $Mg(OH)_2$ and NH_4Cl to be completely dissociated and that NH_4OH is undissociated, calculate the solubility of $Mg(OH)_2$ in one litre of water and its solubility product.

Ans. (1) Solubility = $2{\cdot}75 \times 10^{-4}$ gram mol / litre.

(2) Solubility product = $2{\cdot}08 \times 10^{-11}$.

N. B.— According to the convention of using the formula $(Mg^{\cdot\cdot}) \times 2OH')^2$, the solubility product will be $8\ 33 \times 10^{-11}$.

CHAPTER VI

COLLOIDS AND OTHERS

(A) COLLOIDS; (B) ADSORPTION;

(C) RADIOACTIVITY (D) PHOTOCHEMISTRY

(A) ***Colloids*** :—

1. Size of colloidal particle : (methods).

   (a) Direct method; (b) Velocity of setting; (c) Absorption of light by colloidal particle.

2. Charge on a colloidal particle.

3. Gold Number.

4. Application of colloids to determine Avogadro's Number.

1. Size of a colloidal particle :—

(a) Counting the number of particles with the help of a Zeiss hæmocytometer.

(b_1) Velocity of setting : under gravity.

$$v_0 = \frac{2}{9} \cdot \frac{a^2 g (d - \rho)}{\eta}$$

where v_0 = velocity in cm. / sec.,
a = radius of the particle,
g = gravity,
d = density of the particle,
ρ = density of the medium,
η = viscosity of the medium.

(b_2) The momentum of the particles when subjected to a centrifuge.

$$a = \sqrt{\frac{9}{2} \quad \frac{\eta \log_e \frac{x_2}{x_1}}{(d - \rho) w^2 (t_2 - t_1)}}$$

where w = angular velocity,

$x_1 - x_2$ = distance travelled by the particle,

$t_2 - t_1$ = time,

a, d, ρ, η have the same significance as in the above equation in b_1.

(c) Absorption of light.

$$a = \frac{\sqrt{3}}{4 \pi n} \lambda,$$

where a = radius of the particle,

n = refractive index of the medium,

λ = wave length.

2. **Charge on a colloidal particle :**

(a) Lamb's formula

$$e = V \frac{r^2}{d} K,$$

where e = the change,

r = radius of the particle,

V = P. D. between the particle and water,

K = Dielectric constant of water,

d = distance (in cms.) between two electric layers.

(b) Stoke's formula :

$$e = \frac{6 \pi \eta r v}{X}$$

where e = the charge,

η = the viscosity of water,

r = radius of the particle,

v = velocity of the particle in cm. / sec.,

X = P. D. (Potential difference).

(c) Coagulation by the addition of an electrolyte till the isoelectric point is reached.

3. Gold Number :

"The gold number of a protecting colloid is the number of milligrams of the colloid required to protect 10 c. c. of a stable gold solution containing 0·0053 per cent. of gold from the coagulating action of 1 c. c. of a 10 per cent. solution of sodium chloride".

4. Avogadro's Number :

The behaviour of colloidal particle is used to determine it.

$$2.303 \frac{RT}{N} \log \frac{n_0}{n} = \frac{4}{3}\pi a^3 g (\Delta - \delta) h$$

where n_0 and n = number of granules per unit volume at two layers,

h = distance between these levels,

Δ = density of the particle,

δ = density of the medium,

a = radius of the particle,

g = gravity,

N = Avogadro's number,

R = gas constant,

T = temp. in absolute units.

The most accurate method of determining Avogadro's number is that of Millikan who determines the charge e on an oil particle. An ion, also carries the same charge and since, to discharge a gram ion, 96540 coulombs are required,

$$\text{Avogadro's number} = \frac{96540}{e}$$

(B) *Adsorption :—*

(i) For a gas :

$$\frac{x}{m} = ap^{\frac{1}{n}}$$

where x = mass of the gas adsorbed,
m = mass of the adsorbent,
p = pressure of the gas,
a, n = constants.

(ii) For a solution :

p is replaced by c in the above equation, and is equal to equilibrium concentration. The equation then becomes

$$\frac{x}{m} = ac^{\frac{1}{n}}$$

The equations in (i) and (ii) are called *adsorption isotherms.*

(C) ***Radioactivity*** :—

Radioactive decomposition is a unimolecular reaction, and can be represented by the following equation :

$$\log c_1 = \log c_0 - \frac{\lambda t}{2 \cdot 3} \quad \text{or} \quad \lambda = \frac{2 \cdot 3}{t} \log \frac{c_0}{c_1}.$$

where c_0 = initial concentration,
c_1 = concentration after a time t,
t = time,
λ = constant.

The half life period is the time when c_1 is $\frac{1}{2}c_0$ and is given by the equation :

$$t = \frac{2 \cdot 3}{\lambda} \times \log \frac{c_0}{\frac{1}{2} c_0}$$

$$= \frac{2 \cdot 3 \times \log 2}{\lambda}.$$

Half life $= \dfrac{0 \cdot 6923}{\lambda}$ = average life $\times$ 0·6923, because *the average life* is the reciprocal of λ *i. e.* $\dfrac{1}{\lambda}$.

(D) ***Photochemistry*** :—

Einstein's Law of Photochemical Equivalence : When light rays bring about a chemical reaction for a molecule that decomposes, or for two atoms or molecules that combine, one quantum of light of appropriate wave length is absorbed, or

$$\frac{\text{Number of molecules decomposed}}{\text{Number of quanta absorbed}} = \gamma \quad (\text{Quantum Efficiency}).$$

Quanta of light $= h\nu$

where $h = 6{\cdot}548 \times 10^{-27}$ Planck's constant,

$\nu =$ frequency of light

$$i.e. \quad = \frac{3 \times 10^{10}}{\lambda \text{ (wave length in cms.)}}.$$

This relation is true only for the primary reaction; because usually the products of the primary reaction are in an activated condition and react further. Einstein's Law may be taken to be followed, if

$$\frac{\text{Number of molecule decomposed}}{\text{Number of quanta absorbed}} \approx 2 \text{ or } 3.$$

Problems with Solution

Problem 280. Bredig prepared a silver solution containing 0·068 milligram per 100 c. c. which on dilution to 100 litres showed the presence of 300 particles (average) per 0·1 cu. mm. The specific gravity of silver is 10·5. Determine the radius of the particle.

Solution : The weight of silver particle in 0·1 cu. mm.

$$= \frac{0{\cdot}068}{100 \times 1000 \times 1000 \times 10} \text{ milligram.}$$

$$= 6{\cdot}8 \times 10^{-11} \text{ milligram}$$

$$\text{or} \quad = 6{\cdot}8 \times 10^{-14} \text{ g.}$$

$\therefore$ the total volume $= \dfrac{6{\cdot}8 \times 10^{-14}}{10{\cdot}5}$ c. c.

$\therefore$ the volume of one particle $= \dfrac{6{\cdot}8 \times 10^{-14}}{10{\cdot}5 \times 300}$

$$= \frac{6{\cdot}8 \times 10^{-16}}{31{\cdot}5}$$

If a be the radius of the particle

$$a = \sqrt[3]{\frac{3 \times 6{\cdot}8 \times 10^{-16}}{4 \times \pi \times 31{\cdot}5}}$$

$$= 1{\cdot}727 \times 10^{-6} \text{ cm.}$$

Ans. The mean radius of the particle is $1{\cdot}727 \times 10^{-6}$ cm.

Problem 281. A silver particle in a solution in water falls under gravity with a velocity of 2×10^{-5} cm / sec. Calculate the radius of the particle. Density of silver = 10·5 and viscosity of water = 0·01.

Solution : $v_0 = \dfrac{2(d - \rho) g \cdot a^2}{9 \cdot \eta}$

$$2 \times 10^{-5} = \frac{2 \times 9{\cdot}5 \times 981 \times a^2}{9 \times 0{\cdot}01}.$$

$$\therefore \quad a = \sqrt{\frac{2 \times 10^{-5} \times 9 \times 0{\cdot}01}{2 \times 9{\cdot}5 \times 981}}.$$

$$= 9{\cdot}824 \times 10^{-6}$$

Ans. The radius of the silver particle is $9{\cdot}824 \times 10^{-6}$ cm.

Problem 282. For a gold solution, the maximum absorption occurs at $\lambda = 490\ \mu\mu$ (10^{-8} cm. = $10\ \mu\mu$). Calculate the radius of the gold particle. Refractive index of water = 1·4.

Solution : $a = \dfrac{\sqrt{3}}{4\pi n}\lambda$

$$= \frac{\sqrt{3} \times 49 \times 10^{-6}}{4 \times 3{\cdot}142 \times 1{\cdot}4}$$

$$= 4{\cdot}8 \times 10^{-6} \text{ cm.}$$

Ans. The radius of the gold particle is $4{\cdot}8 \times 10^{-6}$ cm.

Problem 283. From the following data, calculate the charge on the particle in a colloidal platinum solution.

$r = 2 \times 10^{-5}$ cm., $V = 0{\cdot}031$ volts $\left(\frac{0{\cdot}031}{300} \text{ electrostatic}\right)$,

$d = 5 \times 10^{-8}$ cm., $K = 80$ (electrostatic units).

Solution : $e = \frac{Vr^2}{d} K$

$$= \frac{0{\cdot}031 \times (2 \times 10^{-5})^2 \times 80}{300 \times 5 \times 10^{-8}}$$

$$= 6{\cdot}61 \times 10^{-5} \text{ (electrostatic units).}$$

Ans. The charge on the particle is $6{\cdot}61 \times 10^{-5}$ (electrostatic units).

Problem 284. 100 c. c. of a colloidal solution of silver containing 6·5 milligrams of the metal required 26×10^{-6} g of Al (as a soluble salt) to reach the isoelectric point. The mean average radius of the particles was found to be $1{\cdot}7 \times 10^{-5}$. If the sp. gr. of silver is 10·5, calculate the charge on the particle.

Solution : The total volume of silver $= \frac{6{\cdot}5}{1000 \times 10{\cdot}5}$ c. c.

$$= 6{\cdot}19 \times 10^{-4}.$$

The volume of a single particle $= \frac{4}{3} \pi r^3$.

$$= \frac{4 \times 3{\cdot}142 \times (1{\cdot}7 \times 10^{-5})^3}{3}$$

$$= 2{\cdot}05 \times 10^{-14}.$$

The number of particles in 100 c. c. of the solution

$$= \frac{6{\cdot}19 \times 10^{-4}}{2{\cdot}05 \times 10^{-14}}$$

$$= 3 \times 10^{10}$$

The charge carried by 26×10^{-6} gram of Al

$$= \frac{3 \times 96540 \times 26 \times 10^{-6}}{27}$$

$$= 0{\cdot}280 \text{ coulomb.}$$

The opposite charge carried by a single particle

$$= \frac{0{\cdot}280}{3 \times 10^{10}}$$

$$= 9{\cdot}3 \times 10^{-12} \text{ coulombs.}$$

Ans. The charge on the particle is $9{\cdot}3 \times 10^{-12}$ coulombs.

Problem 285. For a colloidal silver solution, Burton found: radius of the particle $= 5{\cdot}77 \times 10^{-6}$; the velocity in cms. per second under a gradient of 1 volt per cm. $= 23{\cdot}6 \times 10^{-5}$ cm. Calculate the charge on the particle.

Solution : $e = \frac{6\pi\eta rv}{X}$.

Substituting the values of the respective symbols in the above equation, we get

$$e = 6 \times 3{\cdot}142 \times 0{\cdot}01 \times 5{\cdot}77 \times 10^{-6} \times 23{\cdot}6 \times 10^{-5} \times 300$$

$$= 7{\cdot}70 \times 10^{-8}.$$

Ans. The charge on the particle is $7{\cdot}70 \times 10^{-8}$.

Problem 286. Perrin gives the following data for the gamboge solution: Radius of the particle $= 0{\cdot}212\,\mu$. The difference of the density $(\Delta - \delta)$ between the material of the granules and water $= 0{\cdot}2067$.

Temperature 20° C.

μ, Level	$5\,\mu$	$35\,\mu$	$65\,\mu$	$95\,\mu$
Concentration of granules	100	47	22·6	12.

Calculate the Avogadro's Number.

Solution : The formula to be employed is

$$2{\cdot}303 \frac{RT}{N} \log\frac{n_0}{n} = \frac{4}{3} \pi a^3 g (\Delta - \delta) h.$$

$$\therefore \quad N = \frac{2{\cdot}303\, RT \log \frac{n_0}{n} \times 3}{4 \times \pi a^3 g (\Delta - \delta) h}$$

$$= \frac{2{\cdot}303 \times 8{\cdot}317 \times 10^7 \times 293 \times \log \frac{100}{47} \times 3}{4 \times 3{\cdot}142 \times (0{\cdot}212 \times 10^{-4})^3 \times 981 \times 0{\cdot}2067 \times 30 \times 10^{-8}}.$$

$$= 75{\cdot}78 \times 10^{22}.$$

The value of N for $\log \frac{47}{22{\cdot}6} = 73{\cdot}50 \times 10^{22}$.

The value of N for $\log \frac{22{\cdot}6}{12} = 63{\cdot}54 \times 10^{22}$.

Ans. The mean value of N is $70{\cdot}94 \times 10^{22}$.

Problem 287. For the adsorption of Argon by cocoanut charcoal, Miss Humphrey found $a = 3{\cdot}698$ and $\frac{1}{n} = 0{\cdot}6024$. Calculate the amount of the gas adsorbed at 12·9 cms. mercury pressure by a unit mass of charcoal.

Solution : The formula to be employed is

$$\frac{x}{m} = ap^{\frac{1}{n}} \quad \text{(adsorption isotherm)}$$

$$= 3{\cdot}698 \times 12{\cdot}9^{0{\cdot}6024}$$

$$= 17{\cdot}24.$$

Ans. The amount (in grams) of Argon adsorbed is 17·24.

Problem 288. In a space containing a radioactive substance, the current (the current when a high potential is used is independent of the potential used and is called saturation current) strength under a high potential is 58·41 (arbitrary) units at a certain time and 13·36 units after 200 hours. Calculate from the data (i) the radio-active constant, (ii) the half life, and (iii) the average life of the radio-active element.

Solution : $\log c_1 = \log c_0 - \frac{\lambda t}{2{\cdot}3}$.

(i) The radio-active constant :

$$\lambda = \frac{2{\cdot}3}{t} (\log c_0 - \log c_1)$$

$$= \frac{2{\cdot}3}{200} (\log 58{\cdot}41 - \log 13{\cdot}36)$$

$$= \frac{2{\cdot}3}{200} (1{\cdot}7665 - 1{\cdot}1259)$$

$$= \frac{2{\cdot}3 \times 0{\cdot}6406}{200}$$

$$= 0{\cdot}007368.$$

(ii) The half life $= \frac{2{\cdot}3 \log 2}{\lambda}$

$$= \frac{0{\cdot}6923}{0{\cdot}0073o8}$$

$$= 93{\cdot}96 \text{ hours.}$$

(iii) The average life $= \frac{1}{\lambda}$

$$= \frac{1}{0{\cdot}007368}$$

$$= 136{\cdot}7 \text{ hours.}$$

Ans. (i) The radio-active constant is 0·007368.
(ii) The half life is 93·96 hours.
(iii) The average life is 136·7 hours.

Problem 289. A solution contains 10 milligrams of lead as a soluble salt. It was mixed with Thorium B of 1C000 activity. Pb in the solute is precipitated as $PbCrO_4$. After filtering off $PbCrO_4$, 100 c. c. of the filtrate (it is a saturated solution of $PbCrO_4$) was found to have an activity 4·14. Determine the solubility of $PbCrO_4$ per litre.

Solution : 10000 units correspond to 10^{-2} gram of Pb.

4·14 units correspond to $4{\cdot}14 \times 10^{-6}$ g of Pb.

∴ 100 c. c. will contain $4{\cdot}14 \times 10^{-6}$ g of Pb,

or $6{\cdot}46 \times 10^{-6}$ g of $PbCrO_4$.

Ans. 1000 c. c. will contain $6{\cdot}46 \times 10^{-5}$ gram of $PbCrO_4$.

Problem 290. When γ–rays energy 2·6 m. e. v.* strike a deuteron atom, a hydrogen atom having 0·25 m. e. v. energy and a neutron are produced. Assuming that the neutron has the same energy as that of hydrogen *i. e.*, 0·25 m. e. v., find the weight of neutron. The weight of the hydrogen ion = 1·0081 and that of deuteron is 2·0147.

Solution : $^{2}_{1}D + \gamma\text{–rays } (2{\cdot}6 \text{ m. e. v.}) = {}^{1}_{1}H + {}^{1}_{0}n.$

Energy of γ–rays absorbed

$$= 2{\cdot}6 \text{ m. e. v.} - (0{\cdot}25 \text{ m. e. v. of } {}^{1}_{1}H + 0{\cdot}25 \text{ m. e. v. of } {}^{1}_{0}n)$$

$$= 2{\cdot}6 \text{ m. e. v.} - 0{\cdot}50 \text{ m. e. v.}$$

$$= 2{\cdot}1 \text{ m. e. v.}$$

The mass of γ–rays absorbed $= 2{\cdot}1 \times 0{\cdot}00107 = 0{\cdot}00225$ g.

$\therefore$ The total mass available $= 2{\cdot}0147 + 0{\cdot}00225 = 2{\cdot}01695$ g.

$$\therefore \text{ mass of } {}^{1}_{0}n = \text{the total mass} - \text{the mass of } {}^{1}_{1}H$$

$$= 2{\cdot}01695 - 1{\cdot}0081$$

$$= 1{\cdot}00885$$

Ans. Weight of neutron is 1·00885.

Problem 291. The density of sodium chloride crystals is 2·17. There are 4 molecules of sodium chloride in the unit cell of the crystals. Calculate the length of the unit cell, given that the atomic weights of Na and Cl are respectively 22·99 and 35·457, and Avogadro's number is $6{\cdot}03 \times 10^{23}$.

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* (i) e. v. $= 1{\cdot}59 \times 10^{-12}$ ergs.

(ii) Energy of 1 atom of H $= \dfrac{9 \times 10^{20}}{6{\cdot}1 \times 10^{23}} = 1{\cdot}49 \times 10^{-3}$ ergs.

(iii) m. e. v. $= \dfrac{10^{6} \times 1{\cdot}59 \times 10^{-12}}{1{\cdot}49 \times 10^{-3}} = 0{\cdot}00107$ g.

Solution : The Lattice* contains 4 NaCl molecules but the unit cell is $\frac{1}{8}$ of the lattice model, and therefore contains $\frac{4}{8}$ NaCl molecule or $\frac{NaCl}{2}$ (Fig. 5). One Avogadro's number, therefore, represents two unit cells or a gram-molecule contains $2 \times 6{\cdot}03 \times 10^{23}$ unit cells. The mass of the unit cell

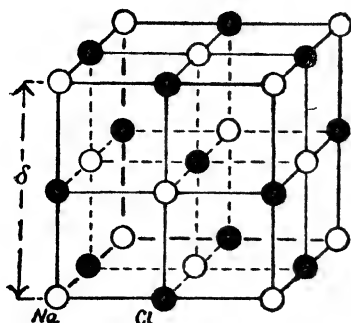



Fig. 5

Lattice of the NaCl crystal

$$= \frac{58{\cdot}447}{2 \times 6{\cdot}03 \times 10^{23}}$$

$$= \frac{58{\cdot}447 \times 1{\cdot}66 \times 10^{-24}}{2}.$$

The density of the salt $= 2{\cdot}17$.

$\therefore$ the mass of the unit cell

$$= 2{\cdot}17 \times (d)^3.$$

$$\therefore 2{\cdot}17 d^3 = \frac{58{\cdot}447 \times 1{\cdot}66 \times 10^{-24}}{2}$$

$$\therefore \quad d^3 = \frac{58{\cdot}447 \times 1{\cdot}66 \times 10^{-24}}{2{\cdot}17 \times 2}$$

$$= 22{\cdot}4 \times 10^{-24}$$

$$\therefore \quad d = 2{\cdot}8 \times 10^{-8}$$

Ans. $d = 2{\cdot}8 \times 10^{-8}$

Problem 292. One c. c. of a concentrated solution of anthracene $C_{14}H_{10}$ in Xylene is illuminated by an arc lamp for one second at a distance of 1 cm. from the light source. The light absorbed has a wave length of 5000 Å and the energy of the light absorbed $= 7{\cdot}2 \times 10^5$ ergs. The amount of anthracene polymerised was 4×10^{-7} gram molecules. Determine the quantum efficiency of the reaction.

Solution : Energy of the light absorbed

$$= \frac{6{\cdot}5 \times 10^{-27} \times 3 \times 10^{18}}{5 \times 10^3} = 3{\cdot}9 \times 10^{-12} \text{ ergs.}$$

Quanta absorbed in 1 sec. $= \frac{7{\cdot}2 \times 10^5}{3{\cdot}9 \times 10^{-12}} = 1{\cdot}8 \times 10^{17}$.

Mols that polymerise $= 4 \times 10^{-7} \times 6{\cdot}1 \times 10^{23}$

$$= 2{\cdot}44 \times 10^{17}$$

---

* The lattice cell is sometimes called the unit cell.

$$\text{Quantum Efficiency} = \frac{2{\cdot}44 \times 10^{17}}{1{\cdot}8 \times 10^{17}} \approx 1{\cdot}3.$$

Ans. The quantum efficiency of the reaction is 1·3.

Problem 293. When γ–rays with an energy of 2·6 m.e.v.* strike on a lead plate, a positron electron pair with an energy of 1·6 m. e. v. is produced. Show that the result approximately supports Einstein's equation $E = mc^2$.

Solution : Mass of an atom of hydrogen

$$= \frac{1}{6{\cdot}03 \times 10^{23}} = 0{\cdot}166 \times 10^{-23} \text{ g}.$$

$\therefore$ Mass of an electron or positron

$$\approx \frac{1}{1760 \text{ to } 1800} \text{ of hydrogen}$$

$$\approx 9 \times 10^{-28}.$$

According to the equation of Einstein, the energy of an electron

$$= 9 \times 10^{-28} \times (3 \times 10^{10})^2 = 81 \times 10^{-8} \text{ ergs}.$$

$$= \frac{81 \times 10^{-8}}{1{\cdot}66 \times 10^{-12}} \text{ e. v.}$$

$$= 0{\cdot}488 \times 10^{6} \text{ e. v.}$$

$$= 0{\cdot}488 \text{ m. e. v.}$$

Ans. The energy consumed in producing an electron positron pair is 2·6 m. e. v. $-$ 1·6 m. e. v. = one m. e. v. $\therefore$ to produce an electron or a positron, energy consumed is about 0·5 m. e. v. and this confirms Einstein's equation.

---

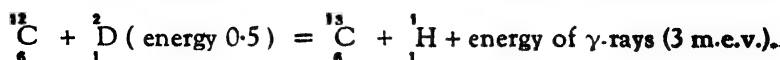
* e = $1{\cdot}59 \times 10^{-19}$ coulombs.

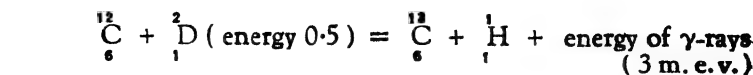
$\therefore$ e. v. = $1{\cdot}59 \times 10^{-19}$ volt coulombs.

= $1{\cdot}59 \times 10^{-19} \times 10^{7}$ ergs. $\because$ 1 volt coulomb = 10^7 ergs

= $1{\cdot}59 \times 10^{-12}$ ergs.

Problem 294. When carbon is struck by accelerated deuterons (energy 0·5 m. e. v.), the following reaction occurs :

$$^{12}_{6}C + {}^{2}_{1}D \text{ (energy 0·5)} = {}^{13}_{6}C + {}^{1}_{1}H + \text{energy of } \gamma\text{-rays (3 m.e.v.)}.$$

Assuming that the energy of $^{13}_{6}C$ and $^{1}_{1}H$ to be 0·0017 in terms of mass, determine the mass of $^{13}_{6}C$. The masses of $^{12}_{6}C$, $^{2}_{1}D$, $^{1}_{1}H$ are 12·004, 2·0147 and 1·0081, respectively.

Solution :

$$^{12}_{6}C + {}^{2}_{1}D \text{ (energy 0·5)} = {}^{13}_{6}C + {}^{1}_{1}H + \text{energy of } \gamma\text{-rays (3 m. e. v.)}$$

		Mass of $^{1}_{1}H$	= 1·0081
Total mass available	$^{12}_{6}C$ = 12·0040	Mass produced from energy of γ–rays	= 0·0032
	$^{2}_{1}D$ = 2·0147		
Mass of energy	= 0·0005	Energy of $^{13}_{6}C + {}^{1}_{1}H$	= 0·0017
Total	14·0192	Total	1·0130

~~14·092~~ = Mass of $^{13}_{6}C$ + 1·0130

$\therefore$ Mass of $^{13}_{6}C$ = 14·0192 − 1·0130.

= 13·0062.

Ans. The mass of $^{13}_{6}C$ is 13·0062.

Problems for Solution

Problem 295. The mean kinetic energy of a molecule at 0°C. is $5{\cdot}621 \times 10^{-14}$ ergs. Taking $R = 83{\cdot}2 \times 10^6$ c.g.s. units, calculate the actual number of molecules in one gram molecule of a gas.

Ans. $4{\cdot}04 \times 10^{23}$.

Problem 296. Given that a coulomb (*i.e.*, $\frac{1}{10}$th of the electro-magnetic unit of electricity) liberates $1{\cdot}036 \times 10^{-5}$ grams of hydrogen, and that "e" $= 4{\cdot}77 \times 10^{-10}$ absolute electrostatic units, calculate the number of atoms in a gram atom. 1 electro-magnetic unit $= 3 \times 10^{18}$ electrostatic unit.

Ans. $60{\cdot}71 \times 10^{22}$.

Problem 297. A two c.c. vessel containing a perfect gas at 27°C. is exhausted to a pressure of 10^{-6} mm. How many molecules remain in the vessel? ($N = 6{\cdot}028 \times 10^{23}$).

Ans. $6{\cdot}446 \times 10^{10}$.

Problem 298. The activity of the radio element falls to half its value in 5 days. Calculate the radio-activity constant (in hours) and the time for the activity to fall to $\frac{1}{10}$th of its maximum value.

Ans. $\lambda = 0{\cdot}00577$; $t = 398{\cdot}6$ hours.

Problem 299. Radium emanation mixed with air was obtained from a solution of radium chloride. Equal quantities were transferred into a testing vessel from time to time. Measurements of the ionisation constant immediately after the introduction of the emanation into the testing vessel gave the following results :—

Time in hours	0	20·8	187·6	354·9	521·9	786·9
Relative intensity of the current	100·0	85·7	24·0	6·9	1·5	0·19.

Calculate (a) the mean value of the velocity constant (monomolecular), and (b) time in hours when the activity is reduced to half.

Ans. (a) $\lambda = 0{\cdot}007705$; (b) $t = 89{\cdot}85$ hours.

Problem 300. The activity of some thorium emanation fell to half its initial value in 60 seconds. What is the radioactive constant (in seconds) of thorium emanation?

Ans. $\lambda = 0{\cdot}01154$.

Problem 301. The density of potassium chloride crystal is 2·005. There are 4 molecules of potassium chloride in the unit cell* of the crystal. Calculate the length of the unit cell, given that the atomic weights of K and Cl are respectively, 39·096 and 35·457, and Avogadro's number is $6{\cdot}03 \times 10^{23}$.

Ans. $3{\cdot}161 \times 10^{-8}$ cm.

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* Refer to foot-note at page 185.

APPENDIX — Reference Tables

CONVERSION TABLE

—	Ergs	Joules Watt – sec.	15° cal.	Litre Atmospheres	Kilo-gram Metre
Erg	—	10^{-7}	$2{\cdot}389 \times 10^{-8}$	$9{\cdot}869 \times 10^{-10}$	$1{\cdot}019 \times 10^{-8}$
Joule	10^{7}	—	$2{\cdot}389 \times 10^{-1}$	$9{\cdot}869 \times 10^{-3}$	$1{\cdot}019 \times 10^{-1}$
Calorie	$4{\cdot}185 \times 10^{7}$	4·185	—	$4{\cdot}131 \times 10^{-2}$	$4{\cdot}268 \times 10^{-1}$
Litre Atmosphere	$1{\cdot}0133 \times 10^{9}$	$1{\cdot}0133 \times 10^{2}$	$2{\cdot}420 \times 10$	—	$1{\cdot}033 \times 10$
Kilo-gram Metre	$9{\cdot}806 \times 10^{7}$	9·806	2·343	$9{\cdot}678 \times 10^{-2}$	—
R (Universal gas constant)	$8{\cdot}317 \times 10^{7}$	8·317	1·987	$8{\cdot}209 \times 10^{-2}$	$8{\cdot}428 \times 10^{-1}$

PRACTICAL UNITS

Gravity	=	980·617 dynes.
Standard Atmosphere—Mercury pressure	=	760mm., Temp. 0°C., at sea level.
Gram calorie	=	The amount of heat required to raise the temp. of 1 gram of water from 14·5°C. to 15·5°C.
Kilo-gram calorie	=	1000 gram calories.
British Thermal unit	=	The amount of heat required to raise the temp. of 1 lb. of water from 1°F to 60°F.
Joule	=	Volt × coulomb = 10^7 ergs.
Watt	=	1 Joule per second.
Board of Trade Unit—Kilowatt hour	=	1000 × 3600 Joules.
Foot-lb. second	=	1·357 watts.
Horse power	=	746 watts.

HEATS OF ATOMISATION OF ELEMENTS

(*Figures are given in Kg. cals. per g atom*)

Element	State	Heat of Atomisation
Hydrogen	Gas	51·5
Oxygen	Gas	59·0
Nitrogen	Gas	104·0
Flourine	Gas	32·0
Chlorine	Gas	28·7
Bromine	Gas	24·9
	Liquid	28·7
Iodine	Gas	18·0
	Solid	25·5
Sulphur	S_2 gas	52·0
	Rhombic	66·8
Carbon	Solid	150·0

SOME OF THE VALUES OF PARACHOR

H	17·1	Triple bond	46·6
C	4·8	Double bond	23·2
O	20·0	3 – ring	16·7
N	12·5	4 – ring	11·6
S	48·2	5 – ring	8·5
Cl	54·3	6 – ring	6·1
Br	68·0	Single bond	0·0 (arbitrary)
I	91·0	Semipolar double bond	– 1·6
P	37·7	O_2 in esters	60·0.

NORMAL ELECTRODE POTENTIALS (25°)

$Li^{\cdot}$	– 2·958	$H^{\cdot}$	± 0·0
$Rb^{\cdot}$	– 2·924	$Cu^{\cdot\cdot}$	+ 0·345
$K^{\cdot}$	– 2·922	O_2 (OH')	+ 0·398
$Na^{\cdot}$	– 2·713	I'	+ 0·536
$Zn^{\cdot\cdot}$	– 0·758	$Hg_2^{\cdot\cdot}$	+ 0·799
$Fe^{\cdot\cdot}$	– 0·441	$Ag^{\cdot}$	+ 0·800
$Cd^{\cdot\cdot}$	– 0·398	H_2 (OH')	– 0·828
$Sn^{\cdot\cdot}$	– 0·136	Br'	+ 1·066
$Pb^{\cdot}$	– 0·122	Cl'	+ 1·359
$Fe^{\cdot\cdot}$	– 0·045	F'	+ 1·9

MOBILITIES (*absolute velocities*)

U and V of a number of ions at 18°C. (in cm^2 sec^{-1} $volt^{-1}$).

CATION	U	ANION	V
$H^{\cdot}$	33 × 10^{-4}	OH'	18·2 × 10^{-4}
Li	3·5 × 10^{-4}	Cl'	6·85 × 10^{-4}
$Na^{\cdot}$	4·6 × 10^{-4}	Br'	7·0 × 10^{-4}
$K^{\cdot}$	6·75 × 10^{-4}	I'	6·95 × 10^{-4}
$Ag^{\cdot}$	5·7 × 10^{-4}	NO_3'	6·5 × 10^{-4}
$NH_4^{\cdot}$	6·7 × 10^{-4}	MnO_4'	5·6 × 10^{-4}
$Zn^{\cdot\cdot}$	4·8 × 10^{-4}	SO_4''	7·1 × 10^{-4}
$Fe^{\cdot\cdot}$	4·8 × 10^{-4}	$(COO)_2''$	6·6 × 10^{-4}
$Fe^{\cdot\cdot\cdot}$	4·6 × 10^{-4}	CO_3''	6·2 × 10^{-4}

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